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Abstract

Ten new triterpenoids were isolated from the exudate of *Salvia argentea* L. var. *aurasiaca* (Pomel) Batt. & Trab. Their structures were elucidated by 1D and 2D NMR and HRESIMS analyses as 11α-methoxyurs-12-ene-1β,3β,15α-triol (**1**), Urs-12-ene-1β,3β,11α,15α-tetraol (**2**), 11α-methoxyurs-12-ene-1β,3β-diol (**3**), 1β,3β,15α-trihydroxy-11α-methoxyurs-12-en-28-al (**4**), 1β,3β,15α-trihydroxyurs-12-en-28-al (**5**), urs-12-ene-1β,3β,15α,28-tetraol (**6**), 11α-methoxyurs-12-ene-1β,3β,28-triol (**7**), 13β,28-epoxyurs-12-ene-1β,3β-diol (**8**), urs-12-ene-3β,7β,15α,28-tetraol (**9**) and olean-12-ene-3β,7β,15α,28-tetraol (**10**). A chemotaxonomic approach of the triterpenoids of *Salvia* species show that triterpenoids from the exudate of *Salvia argentea* var. *aurasiaca* (pomel) Batt. & Trab., provide some new features, such as hydroxylation at C-15, and hydroxylation at C-7. On the basis, *S. argentea* L. var. *aurasiaca* (Pomel) Batt. & Trab., is quite different from *S. argentea* L.

Keywords: *Salvia argentea* L. var. *aurasiaca;* Ursane Triterpenoids; Exudate; Chemotaxonomy

Introduction

Plants of the genus *Salvia* (Lamiaceae) are well known for their richness in flavonoids (Lu and Foo, 2002), diterpenoids (Kabouche and Kabouche, 2008), triterpenoids and other compounds (Wu et al., 2012). These secondary metabolites have been found to have some interesting biological activity (Wu et al., 2012). In a continuation of our studies on *Salvia* species (Kabouche et al., 2005, 2007, 2008; Kolak et al., 2009) we report herein the first phytochemical investigation of the exudate of *Salvia argentea* L. var. *aurasiaca* (Pomel) Batt. & Trab. Ten new triterpenoids (**1-10**) (figure 1), together with the known compound urs-12-ene-1β, 3β, 11α-triol (Huang et al., 2008), were obtained.

2. Results and discussion

Compound **1** was obtained as a white, amorphous powder. Its molecular formula $C_{31}H_{52}O_4$ was determined on the basis of its HRESIMS spectrum (*m/z* 511.3774 $[M+Na]^+$, calcd 511.3763). The ^1H NMR spectrum exhibited an olefinic proton at δ 5.51 (1H, d, *J* = 3.5 Hz), four protons at δ 3.32 (1H, dd, *J* = 12.3 and 4.4 Hz), δ 3.43 (1H, *J* = dd, 10.4 and 4.0 Hz), δ 4.11 (1H, dd, *J* = 8.5 and 3.5 Hz) and δ 4.17 (1H, dd, *J* = 11.4 and 5.9 Hz) indicative of oxygenated methines, a methoxyl singlet (δ 3.41), six tertiary methyl groups (δ 0.82, 0.88, 1.01, 1.09, 1.13, and 1.20), and two secondary methyl groups [δ 0.94 (d, *J* = 6.3 Hz) and δ 0.97 (d-like)]. In addition, the ^{13}C NMR spectrum, displayed four oxygenated methines at δ 68.0, 75.6, 76.0, and 76.7, eight methyls at δ 13.0, 15.2, 16.8, 17.6, 19.0, 21.3, 28.1, and 29.2, a methoxyl at δ 54.1, and two olefinic carbons at δ 123.3 and 146.6. These data suggested that **1** was an 11-methoxyurs-12-ene derivative (Mahato and Kundu, 1994) similar to olibanumol M (11α-methoxyurs-12-en-3β-ol), except for the replacement of two methylenes by two a oxymethines (Morikawa et al., 2010). H-3, [δ 3.32 (dd, *J* = 12.3, 4.4 Hz)] and H-11 [δ 4.11 (1H, dd, *J* = 8.5, 3.5 Hz)] were readily identified from literature data. The assignment of H-11 was confirmed by

its COSY correlations with H-12 [δ 5.51 (d, *J* = 3.5 Hz)] and H-9 [δ 1.81 (d, *J* = 8.5 Hz)] and its HMBC correlation with the methoxyl carbon. The first additional oxymethine (δ 3.43, dd, *J* = 10.4, 4.0 Hz) was then assigned as C-1 as a result of the downfield shifts of C-2 (δ 35.7) and C-10 (δ 44.7), HMBC correlations between C-1 (δ 76.7) and the protons H-3 (δ 3.32) and H-25 (1.09) and COSY correlations between H-2 (δ 1.73 and 1.91)/H-3 and H-2 /H-1. The second additional oxymethine (δ 4.17, dd, *J* = 11.4, 5.9 Hz) was assigned as C-15 as a result of the downfield shifts of C-14 (δ 47.5) and C-16 (δ 38.9) and HMBC correlations of H-15/C-13 (δ 146.6), C-14 (δ 47.5), and C-27 (δ 16.8). Thus compound **1** is an 11-methoxyurs-12-ene-1,3,15-triol.

The coupling constants of H-1 (10.4, 4.0 Hz) and H-3 (12.3, 4.4 Hz) indicated their α-axial orientations. This was confirmed by the NOE correlations observed between H-3α /H-5α and H-23α and between H-1α /H-9α (Topçu et al., 2004). The methoxyl group at C-11 and the hydroxyl group at C-15 were shown to be α-oriented by the NOESY correlations between H-11/H-26 and H-15/H-25 and H-26. Furthermore, the NOE effect between H-12/H-18 clearly confirmed the expected *cis* D-E ring fusion. The full assignments of the ^{1}H NMR and ^{13}C NMR data of **1** are listed in Table 1. On the basis of the above evidence, the structure of compound **1** was established as 11α-methoxyurs-12-ene-1β,3β,15α-triol.

Compound **2** was obtained as a white powder with the molecular formula, $C_{30}H_{50}O_4$, (HRESIMS *m/z* 497.3615 $[M + Na]^+$, calcd 497.3607). The ^{1}H and ^{13}C NMR spectra of **2** were similar to those of compound **1** except for the absence of signals for a methoxyl group (Table 1). The presence of a hydroxyl group at C-11 instead of a methoxyl was apparent from the chemical shifts of C-11 (δ 67.4), C-9 (δ 56.9) and C-12 (δ 129.6). The NOE effects observed for protons H-1, H-3 and H-15 were identical to those observed in compound **1**. Therefore, the structure of compound **2** was established as urs-12-ene-1β,3β,11α,15α-tetraol.

Compound **3** was found to have the molecular formula $C_{31}H_{52}O_3$, (HRESIMS *m/z* 495.3805 $[M + Na]^+$, calcd for 495.3814), one oxygen fewer than compound **1**. Comparison of their NMR spectroscopic data revealed that **3** differed only in ring D. The shielding of C-14 (δ 41.9) and C-16 (δ 27.9) and the deshielding of C-27 (δ 22.4) indicated the absence of hydroxyl at C-15. This was confirmed by the chemical shifts of C-15 (δ 27.2) and 2H-15 (δ 1.10 and 1.75). Me-27 showed a correlation with C-15 in the HMBC spectrum. Thus compound **3** is 11α-methoxyurs-12-ene-1β,3β-diol.

Compound **4**, a white amorphous solid, had a molecular ion peak at *m/z* 525.3554 $[M + Na]^+$ (calcd for $C_{31}H_{50}O_5$, 525.3556) in the HRESIMS. Its NMR spectroscopic data differed from those of compound **1** only in rings D and E. Me-28 was replaced by an aldehyde (δ_C 207.9, δ_H 9.32 (s)]. This was confirmed by HMBC correlations from H-18, H-16 and H-22 to C-28. A NOE interaction between the aldehyde proton and H-18 (δ 2.16) indicated the expected β orientation of the aldehyde function. Other NOE effects confirmed the β orientation of the hydroxyl groups in positions 1 and 3 and the α orientation of the methoxyl group in position 11, as in **1**. Thus compound **4** was identified as 1β,3β,15α trihydroxy-11α-methoxyurs-12-en-28-al.

Compound **5** was obtained as a white powder with the molecular formula $C_{30}H_{48}O_4$, (HRESIMS *m/z* 495.3440 $[M + Na]^+$, calcd 495.3450). The ^1H and ^{13}C NMR spectra of compound **5** differed from those of **4** only in ring C due to the absence of the C-11 methoxyl group. In the ^{13}C NMR spectrum of **5**, C-11 appeared at δ 26.9 while the corresponding protons (δ 2.11 and 2.57) correlated with H-12 in the COSY spectrum. Thus the structure of **5** was established as 1β,3β,15α-trihydroxyurs-12-en-28-al.

The positive HRESIMS of compound **6** gave a pseudomolecular ion peak at *m/z* 497.3600 $[M + Na]^+$, in agreement with the molecular formula $C_{30}H_{50}O_4$. The NMR data of **6** were similar to those of **5** apart from the fact that the C-28 aldehyde of **5** was replaced by a

primary hydroxyl group [δ_C 70.3; δ_H 3.52 (d, *J* = 10.9 Hz) and δ_H 3.25 (d, *J* = 10.9 Hz)] (Table 2). HMBC correlations from 2H-28 to C-16, C-18 and C-22 confirmed the presence of a C-28 hydroxymethylene group. NOESY correlations from 2H-28 to H-18, H-1 to H-9 and H-3 to H-5 supported the relative configuration of **6** as shown. Thus compound **6** is urs-12-ene-1β,3β,15α,28-tetraol.

The NMR data of compound **7**, $C_{31}H_{52}O_4$ (HRESIMS *m/z* 511.3752 $[M + Na]^+$), were very similar to those of **3**, apart from the replacement of Me-28 by a hydroxymethylene group (Tables 1 and 2). The attachment of the hydroxymethylene group to C-17 was readily confirmed by the HMBC correlations from 2H-28 to C-22, C-18, and C-16. As expected, a NOE interaction was observed between H-28 and H-18. Thus compound **7** is 11α-methoxyurs-12-ene-1β,3β,28-triol.

The molecular formula of compound **8** was established as $C_{30}H_{48}O_3$ (HRESIMS *m/z* 479.3497). The ^{1}H NMR spectrum revealed signals for a ring A 1β,3β-diol system and two vinyl protons [δ 5.46 (dd, *J* = 10.6 and 3.0 Hz. H-11) and δ 6.79 (dd, *J* = 10.6 and 1.0 Hz, H-12], suggesting an 11,12-double bond. H-11 and H-12 both correlated in the HMBC spectrum with C-9 and an oxygenated quaternary carbon (C-13, δ 84.7). The latter and the C-28 oxygenated methylene group [δ_H 3.23 (dd, *J* = 6.7 and 1.5 Hz) and 3.68 (d, *J* = 6.7 Hz); δ_C 69.7] indicated the presence of a 28,13β-epoxide moiety (Gonzalez et al., 1990) (Table 2). Correlations in the NOESY spectrum were consistent with the relative configuration as in **8**. Thus compound **8** is 13β,28-epoxyurs-12-ene-1β,3β-diol.

Compound **9** had the same molecular formula, $C_{30}H_{50}O_4$ (*m/z* 497.3605 $[M + Na]^+$), as compound **6**. Its spectroscopic properties revealed that it was an urs-12-ene tetraol (Table 3) (Mahato and Kundu, 1994), closely related to **6** apart from the substitution in rings A and B. The presence of hydroxyl groups at C-3 and C-7 was readily established by HMBC correlations from Me-23 and Me-24 to C-3 (δ 78.7) and from Me-26 and H-5 to C-7 (δ 72.0). The β

orientation of these hydroxyl groups were apparent from inspection of coupling constants and from the NOE correlations between H-7/H-5 and H-7/H-27 and between H3/H5 and H3/H23. Thus, compound **9** is urs-12-ene-3β,7β,15α,28-tetraol.

Compound **10** was isomeric with compound **9**. The ^{13}C chemical shifts of the trisubstituted double bond [δ 125.6 (C-12), δ 146.0 (C-13)] and the lack of secondary methyl resonances suggested an olean-12-ene skeleton (Mahato and Kundu, 1994). The spectroscopic data of **10** were essentially the same as those of **9** except for the ring E resonances associated with the methyl groups Me-29 and Me-30 (Table 3). Analysis of the NOESY spectrum confirmed the relative stereochemistry as shown. Thus compound **10** is olean-12-ene-3β,7β,15α,28-tetraol.

3. Chemotaxonomic approach

Only 140 of the 900 recorded *Salvia* species have been subjected to phytochemical examination, and about 60 are rich in triterpenoids (Topçu, 2006). The main more complex pentacyclic triterpenoids reported are oleananes, ursanes and lupanes, with only three taraxeranes from two Spanish species, *S. broussonetti* (Fraga et al., 1991; Gonzalez et al., 1971) and *S. palaefolia* (Gonzalez et al., 1989, 1991), and two cycloartanes from two Chinese species, *S. przewalskii* (Wang et al., 1988; Chen et al., 2003) and *S. trijuga* (Lu and Luo, 1996; Yang et al., 2005; Pan et al., 2010). Friedelane and glutinane derivatives have been found only in two species, *S. glutinosa* (Topçu et al., 1997) and *S. viridis* (Romanova et al., 1972). Dammaranes are less common, with only nine examples, isolated from five species, namely *S. aspera* (Esquivel et al., 2002), *S. barrelieri* (Kolak et al., 2009), *S. bicolor* (Valverde et al., 1985), *S. hierosolymitana* (Pedreros et al., 1990) and *S. santolinifolia* (Ahmad et al., 2008). Seven baccharane triterpenoids have been reported from *S. buccharica* (Ahmad et al., 1999) and *S. hydrangea* (Farimani et al., 2011).

The abundance and distribution of pentacyclic triterpenoids in different *Salvia* species is highly variable. For example, oleananes are present in 52 species and ursanes in 46 species while lupanes are found in 28 species (Table S1, supporting information). However, most of the lupanes occur in only 6 species (*S. maccrochlamys* (Topçu et al., 2007), *S. monbretii* (Garcia-Alvarez et al., 1981), *S. phlomoides* (Topçu et al., 2007), *S. pratensis* (Anaya et al., 1989), *S. sclareoides* (Rauter et al., 2005) and *S. wagneriana* (Bisio et al., 2004)).

Although simple oleanane, ursane and lupane derivatives (*e.g* β-amyrin) are found, in many species (Topçu, 2006) more widespread functionalisation is common. For example, the C-28 methyl group is often oxidized to a carboxyl group, less frequently to a CH_2OH group and occasionally appears as an aldehyde (*S. mellifera* (Luis and Andres, 1999; Gonzales et al., 1990), *S. palaestina* (Miski et al. 1983; Ulubelen et al., 1985; Hussein et al., 1997; Al-Jaber et al., 2012), *S. paramiltiorhiza* (Sun et al., 1992) and *S. verticillata* (Ulubelen and Topçu, 1984; Sommez et al., 1997)). Similarly, the common C-3 hydroxyl group is sometimes acetylated and less frequently oxidized to a ketone. Many *Salvia* species contain triterpenoids with a hydroxyl group at C-2 and, less frequently, at C-1 or C-11. It is noteworthy that a hydroxyl group is observed at C-6 of an oleanane from *S. sclareoides* (Rauter et al., 2005) and an ursane from *S. hierosolymitana* (De Felice et al., 2006) and at C-7 of a lupane from *S. pratensis* (Anaya et al., 1989). C-19 hydroxylation occurs in nine triterpenoids, two of which are an ursane and a lupane, while C-21 hydroxylation has been reported in only three compounds, an ursane, an oleanane and a lupane, from *S. nemorosa* (Ulubelen et al., 1994), *S. staminea* (Topçu et al., 2003) and *S. macrochlamys* (Topçu et al., 2007), respectively. The C-22 hydroxylated lupanes and oleananes are not widely represented in the *Salvia* genus; some of these compounds have been isolated from *S. wagneriana* (Bisio et al., 2004), *S. macrochlamys* (Topçu et al., 2007) and *S. leucantha* (Mukherjee et al., 1988, 1992). In addition, *Salvia* oleananes and ursanes generally contain a C-12/C-13 double bond though six Δ^{18} derivatives have been reported (Xu et al., 2004).

Furthermore, pentacyclic triterpenoids bearing a hydroxyl group at C-11 may undergo dehydration to give the corresponding C-9(11), C-12-diene.

On the basis of this chemotaxonomic study, it appears that triterpenoids from the exudate of *Salvia argentea* var. *aurasiaca* (pomel) Batt. & Trab., provide some new features, such as hydroxylation at C-15, observed for the first time in the *Salvia* genus, and hydroxylation at C-7, reported for the first time in *Salvia* oleananes and ursanes though previously observed in a lupane from *S. pratensis*. The presence of a C-28 aldehyde group is less common. The 13β,28-epoxide moiety is frequently observed in triterpenoids from the Myrsinaceae and Primulaceae (Foubert et al., 2008) but in the *Salvia* genus it is only found in *S. mellifera*.

4. Conclusion

Ten new triterpenoids, with polyhydroxylated ursane and oleanane skeletons, were isolated from the exudate of *Salvia argentea* var. *aurasiaca* (Pomel) Batt. & Trab. The species *S. argentea* L. (Bruno et al., 1987) is similar to *S. kronenburgii* (Topçu et al., 1999, 2004) in terms of its triterpenoid content, namely ursanes and oleananes hydroxylated or acetoxylated at C-1, C-2, C-11 and C-20. All the triterpenoids of *S. argentea* L. possess a hydroxyl or an acetyl group at C-2. However, *S. argentea* var *aurasiaca* (Pomel) Batt. & Trab., is distinguished by the additional hydroxylation of its ursanes and oleananes at C-7, C-15 and/or C-28.

5. Experimental

5.1. General experimental procedure

^{1}H and ^{13}C NMR spectra were recorded in CD_3OD or $CDCl_3$ on a Bruker Avance DRX III 500 spectrometer (^{1}H at 500 MHz and ^{13}C at 125 MHz). 2D experiments were performed using standard Bruker microprograms. HR-ESIMS experiments were performed using a Micromass Q-TOF micro instrument (Manchester, UK). Optical rotations were determined in MeOH with

a Perkin-Elmer 341 polarimeter. TLC was performed on pre-coated silica-gel 60 F254 Merck and detection was revealed by H_2SO_4 50%. CC was carried out on Kieselgel 60 (63-200 mesh) or LiChroprep RP-18 (40-63 µm) Merck. HPLC was performed on a Dionex apparatus equipped with an ASI-100 autosampler, a P580 pump, a diode array detector UVD 340S and a Chromeleon® software. C18 reversed phase column (Phenomenex 250x10 mm, Luna 5µ) was used for semi preparative HPLC with binary gradient eluent (Solvent A, H_2O (pH 2.4 with TFA); Solvent B, MeCN) and a flow rate 3.5 mL/min; the chromatogram was monitored at 205 nm.

5.2. Plant Material

The aerial parts of *Salvia argentea* var. *aurasiaca* (pomel) Batt. & Trab. were collected from Ain El Bey, Constantine County, Algeria in May 2009, and identified by Professor Gerard De Belair. A voucher specimen (LOST Saa.07.10) has been deposited at the herbarium of LOST Laboratory, University of Constantine

5.3. Extraction and Isolation

For the extraction of the secretion product, fresh aerial parts (4.5 kg) were immersed in a mixture of toluene and EtOAc (6:4 v/v) for 20s. After filtration, the extraction solvent was evaporated under reduced pressure to give 43 g of extract. A part of the extract, 14 g, was subjected silica gel VLC, eluting successively with 300 mL of $CHCl_3$/EtOAc (0 %, 10%, 20%, 40%, 60%, 80%, 100%) then with a gradient of EtOAc/MeOH (10%, 20%, 40%, 60%) to give seven fractions (A–G). Fraction D (2.2 g) was subjected CC over R-P C-18 eluting with a gradient of MeOH:H_2O (5:5 to 1:0) to afford 70 fractions. Frs [22-23], eluted with MeCN/H_2O (7:3), were separated by semi-prep HPLC with 45% B for 15 min to give subfraction Fr 9 (R_t = 14.4 min) from which compound **4** (3.7 mg) was obtained by TLC using the elution system

($CHCl_3$:MeOH, 9.5:0.5). Frs [24-31], eluted with MeOH: H_2O (7:3), were purified by semi-prep HPLC with the elution program: 45%-50% of B for 25 min affording compounds **5** (R_t = 28.3 min) (11 mg) and **6** (R_t = 12.8 min) (5 mg). Frs [36-39] (200 mg), eluted with MeOH: H_2O (8:2), were separated by silica gel CC, eluting with a gradient of $CHCl_3$:MeOH (0% to 100% of MeOH), to give compounds **1** (4.4 mg) and Frs **I** and **II**. Fr **I** was further separated by silica gel CC eluting with a gradient of $CHCl_3$/MeOH (0 to 50 %), to yield compound **2** (39.5 mg) and subfraction **Ia** which was combined with fr **II** and purified by semi-prep HPLC using the binary gradient, from 40% to 45% of B, for 30 min yielding compound **10 (**R_t = 16.8 min) (2.9 mg) and a mixture of three ursanes (R_t = 15 min) which was purified by preparative TLC, using $CHCl_3$/MeOH (9.5:0.5 v/v), to give **7** (4.4 mg), **8** (5.9 mg) and **9** (4 mg). Finally, Frs [59-64], eluted with MeOH:H_2O (9.5:0.5), was subjected to silica gel CC, using a gradient of $CHCl_3$:MeOH, to yield compounds **3** (93.1 mg) and the known compound urs-12-ene-1β, 3β, 11α-triol (23.1 mg).

*5.3.1. 11α-methoxyurs-12-ene-1β,3β,15α-triol (**1**)*

White amorphous solid; $[\alpha]^{20}_D$ 10.5 (*c* 0.22, MeOH); for ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) spectroscopic data, see table 1. HR-ESIMS $[M + Na]^+$ *m/z* 511.3774 (calcd for $C_{31}H_{52}O_4Na$, 511.3763).

*5.3.2. Urs-12-ene-1β,3β,11α,15α-tetraol (**2**)*

White amorphous solid; $[\alpha]^{20}_D$ 20 (*c* 0.33, MeOH); for ^{1}H NMR (CD_3OD, 500 MHz) and ^{13}C NMR (CD_3OD, 125 MHz) spectroscopic data, see table 1. HR-ESIMS $[M + Na]^+$ *m/z* 497.3615 (calcd for $C_{30}H_{50}O_4Na$, 497.3607).

*5.3.3. 11α-methoxyurs-12-ene 1β,3β diol (**3**)*

White amorphous solid; $[\alpha]^{20}_{D}$ 16.6 (*c* 0.5, MeOH); for ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) spectroscopic data, see table 1. HR-ESIMS $[M + Na]^+$ *m/z* 495.3805 (calcd for $C_{31}H_{52}O_3Na$, 495.3814).

*5.3.4. 1β,3β,15α trihydroxy-11α-methoxyurs-12-en-28-al (**4**)*

White amorphous solid; $[\alpha]^{20}_{D}$ -7.6 (c 0.29, MeOH); for ^{1}H NMR (CD_3OD, 500 MHz) and ^{13}C NMR (CD_3OD, 125 MHz) spectroscopic data, see table 1. HR-ESIMS $[M + Na]^+$ *m/z* 525.3554 (calcd. for $C_{31}H_{50}O_5Na$, 425.3556).

*5.3.5. 1β,3β,15α-trihydroxyurs-12-en-28-al (**5**)*

White amorphous solid; $[\alpha]^{20}_{D}$ 29.5 (*c* 1.0, MeOH); for ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) spectroscopic data, see table 2. HR-ESIMS $[M + Na]^+$ *m/z* 495.3440 (calcd for $C_{30}H_{48}O_4Na$, 495.3450).

*5.3.6. Urs-12-ene-1β,3β,15α,28-tetraol (**6**)*

White amorphous solid; $[\alpha]^{20}_{D}$ 38 (*c* 0.25, MeOH); for ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) spectroscopic data, see table 2. HR-ESIMS $[M + Na]^+$ *m/z* 497.3600 (calcd for $C_{30}H_{50}O_4Na$, 495.3607).

*5.3.7. 11α-methoxyurs-12-ene-1β,3β,28-triol (**7**)*

White amorphous solid; $[\alpha]^{20}_{D}$ 8.4 (*c* 0.31, MeOH); for ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) spectroscopic data, see table 2. HR-ESIMS $[M + Na]^+$ *m/z* 511.3752 (calcd for $C_{31}H_{52}O_4Na$, 511.3763).

*5.3.8. 13β, 28-epoxy-urs-12-ene-1β,3β-diol (**8**)*

White amorphous solid; $[\alpha]^{20}_{D}$ 42.3 (*c* 0.48, MeOH); for ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) spectroscopic data, see table 2. HR-ESIMS $[M + Na]^+$ *m/z* 479.3497 (calcd for $C_{30}H_{48}O_3Na$, 479.3501).

*5.3.10. Urs-12-ene-3β,7β,15α,28 tetraol (**9**)*

White amorphous solide; $[\alpha]^{20}_{D}$ 35.2 (*c* 0.67, MeOH); for ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) spectroscopic data, see table 3. HR-ESIMS $[M + Na]^+$ *m/z* 497.3605 (calcd for $C_{30}H_{50}O_4Na$, 497.3607).

*5.3.11. olean-12-ene-3β,7β,15α,28-tetraol (**10**)*

White amorphous solid; $[\alpha]^{20}_{D}$ 10 (*c* 0.23, MeOH); for ^{1}H NMR (CD_3OD, 500 MHz) and ^{13}C NMR (CD_3OD, 125 MHz) spectroscopic data, see table 3. HR-ESIMS $[M + Na]^+$ *m/z* 497.3605 (calcd for $C_{30}H_{50}O_4Na$, 497.3607).

Acknowledgements.

The authors are grateful to ANDRS and DGRSDT (MESRS, Algeria) for financial support and to CNRS, Conseil Régional Champagne Ardenne, Conseil Général de la Marne, Ministry of Higher Education and Research (MESR) and EU-programme FEDER to the PlANET CPER project, and to Pr J. Connolly (Glasgow University) for critical reading of the manuscript and linguistic assistance.

Supporting information (Appendix A-C)

The HRESIMS and NMR spectra of compounds **1-10** and the list of functionalized triterpenoids isolated from *Salvia* species (Table S1) can be found, in the online version, at http://

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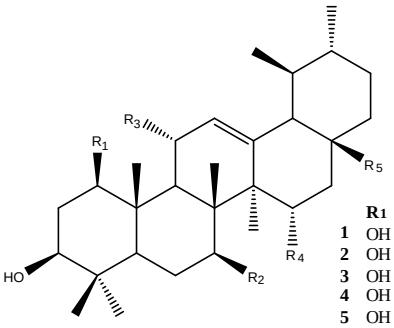

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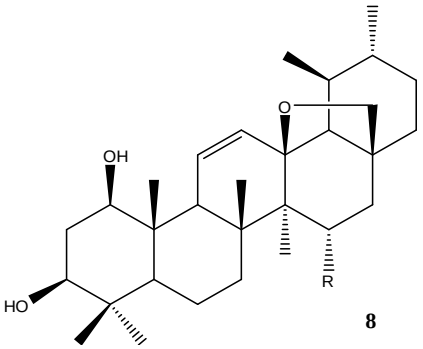
2	OH	H	OH	OH	CH_3
3	OH	H	OCH_3	H	CH_3
4	OH	H	OCH_3	OH	CHO
5	OH	H	H	OH	CHO
6	OH	H	H	OH	CH_2OH
7	OH	H	OCH_3	H	CH_2OH
9	H	OH	H	OH	CH_2OH



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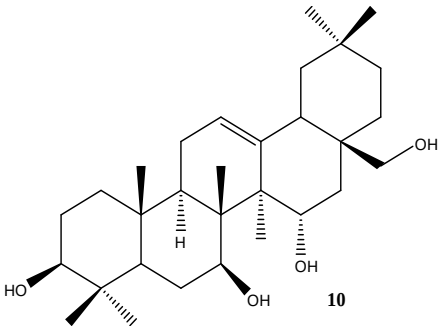

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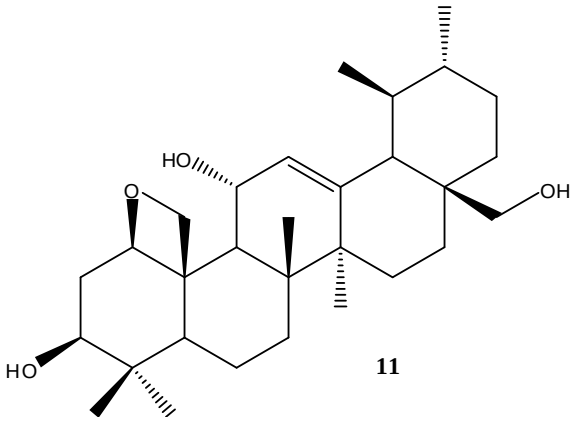

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Table 1

^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectroscopic data of compounds **1**, **3** in $CDCl_3$; 2**, 4** in CD_3OD

Position	**1**		**2**		**3**		**4**	
	δ_H (*J* in Hz)	**δ_C**	**δ_H** (*J* in Hz)	**δ_C**	**δ_H** (*J* in Hz)	**δ_C**	**δ_H** (*J* in Hz)	**δ_C**
1	3.43, *m*	**76.7**	3.51, *dd* (11.3, 4.8)	**78.3**	3.42, *m*	**76.9**	3.44, *dd* (11.4, 4.6)	**78.5**
2	1.73 1.91, *dt* (12.9, 5.3)	**35.7**	1.82, *dt* (12.5, 4.5) 1.76, *m*	**36.3**	1.72 1.90, *dt* (12.9, 4.5)	**35.7**	1.80, *dt* (12.9, 4.6) 1.75, *q* (12.2)	**36.2**
3	3.32, *dd* (12.3, 4.4)	**76.0**	3.25, *dd* (11.9, 4.6)	**76.5**	3.31, *d* (1.9)	**76.0**	3.24, *dd* (12.1, 14.6)	**76.5**
4	-	**39.0**	-	**40.0**	-	**39.0**	-	**40.1**
5	0.66, *dm* (12.1)	**52.1**	0.68, *dm* (11.0)	**53.4**	0.65, *d* (10.2)	**52.4**	0.67, *dd* (11.7, 1.3)	**53.3**
6	1.57, m 1.73	**17.7**	1.60 1.67, *m*	**19.0**	1.54 1.66, *m*	**17.6**	1.64 1.52	**18.7**
7	1.56, *m*	**36.2**	1.61 1.76	**37.2**	1.35 1.51	**33.3**	1.66 1.56	**37.2**
8	-	**45.1**	-	**46.1**	-	**43.8**	-	**46.1**
9	1.81, *d* (8.5)	**52.4**	1.7, *d* (8.6)	**56.9**	1.81, *d* (8.6)	**52.3**	1.81, *d* (8.6)	**53.4**
10	-	**44.7**	-	**45.4**	-	**44.7**	-	**45.8**
11	4.11, *dd* (8.5, 3.5)	**75.6**	4.24, *dd* (8.5, 3.4)	**67.4**	4.13, *dd* (8.6, 3.3)	**75.8**	4.13, *dd* (8.6, 3.5)	**76.6**
12	5.51, *d* (3.5)	**123.3**	5.33, *d* (3.4)	**129.6**	5.41, *d* (2.7)	**122.3**	5.68, *d* (3.6)	**126.1**
13	-	**146.6**	-	**144.7**	-	**146.1**	-	**146.7**
14	-	**47.5**	-	**48.6**	-	**41.9**	-	**49.1**
15	4.17, *dd* (11.4, 5.9)	**68.0**	4.13, *dd* (11.5, 5.8)	**68.5**	1.1 1.75, *m*	**27.2**	4.12, *dd* (11.3, 6.2)	**67.3**
16	1.99, *t* (12.1) 1.19	**38.9**	1.19, *dd* (12.7, 6.8) 2.08, t (12.2)	**39.8**	0.95 2.06, *t* (12.9) 0.94	**27.9**	2.06, *t* (12.5) 1.88, *dd* (12.5, 6.3)	**34.0**
17	-	**33.9**	-	**34.8**	-	**33.6**	-	**50.2**
18	1.44, *d* (11.4)	**58.8**	1.4	**59.6**	1.44, *d* (12.9)	**58.6**	2.16, *d* (10.5)	**53.1**
19	1.35	**38.9**	1.4	**40.5**	1.35	**39.2**	1.48	**39.3**
20	0.95	**39.2**	0.93, *m*	**40.7**	0.95, *m*	**39.4**	1.09	**39.8**
21	1.46, *m* 1.30	**30.8**	1.33 1.45, *m*	**32.0**	1.32 1.44	**31.1**	1.61 1.32	**30.7**
22	1.49, *td* (9.7, 2.8) 1.28	**40.9**	1.33 1.49, *m*	**42.2**	1.33 1.47	**41.3**	1.5 1.28	**32.1**
23	1.01, *s*	**28.1**	1.00, *s*	**28.6**	1.02, *s*	**28.2**	0.99, *s*	**28.7**
24	0.82, *s*	**15.2**	0.81, *s*	**15.8**	0.82, *s*	**15.2**	0.79, *s*	**15.9**
25	1.09, *s*	**13.0**	1.1, *s*	**13.5**	1.09, *s*	**13.0**	1.05, *s*	**13.2**
26	1.13, *s*	**19.0**	1.37, *s*	**19.3**	1.07, *s*	**18.3**	0.84, *s*	**20.1**
27	1.2, *s*	**16.8**	1.21, *s*	**18.0**	1.18, *s*	**22.4**	1.19, *s*	**17.5**
28	0.88, *s*	**29.2**	0.89, *s*	**29.8**	0.83, *s*	**28.6**	9.32, *s*	**207.9**
29	0.94, *d* (6.3)	**17.6**	0.99, *d* (4.3)	**18.1**	0.91, *d* (6.5)	**17.6**	1.05, *d* (6.7)	**17.4**
30	0.97, (*d*-like)	**21.3**	0.99, *d* (4.3)	**21.8**	0.97, *d* (d-like)	**21.4**	1.04, *d* (6.5)	**21.4**
O-CH_3	3.41, *s*	**54.1**	-		3.4	**58.8**	3.42, *s*	**54.5**

[a] overlapped ^{1}H NMR signals are reported without designated multiplicity.

Table 2

^{1}H (500 MHz) and ^{13}C 125 MHz) NMR spectroscopic data of compounds 5-8 (in $CDCl_3$)

Position	5		6		7		8	
	δ_H (*J* in Hz)	δ_c	δ_H (*J* in Hz)	δ_c	δ_H (*J* in Hz)	δ_c	δ_H (*J* in Hz)	δ_c
1	3.46, *dd* (11.5, 4.5)	**79.7**	3.49, *dd* (9.5, 4.5)	**79.8**	3.42, *dt* (10.3-4.0)	**76.9**	3.51	**79.7**
2	1.66 1.86, *dt* (12.3, 4.4)	**37.8**	1.87, *dt* (12.4, 4.5) 1.68	**37.8**	1.73, *q* (12.0) 1.91, *dt* (12.9-4.5)	**35.7**	1.89, *dt* (12.4, 4.4) 1.71, *q* (12.0)	**38.3**
3	3.30, *dd* (4.3, 12.0)	**75.9**	3.31, *dd* (12.0, 4.4)	**75.9**	3.31, *brd* (9.4)	**76.0**	3.28, *dd* (11.9, 4.1)	**75.9**
4	-	**38.7**	-	**38.6**	-	**39.1**	-	**38.9**
5	0.62, *d* (11.3)	**52.6**	0.65, *dm* (11.3)	**52.7**	0.65, *brd* (9.8)	**52.4**	0.60, *dd* (9.6, 5.2)	**52.2**
6	1.52, *m* 1.62	**18.1**	1.66, *m* 1.57, *m*	**18.2**	1.53 1.66	**17.6**	1.64 1.67	**17.2**
7	1.69 1.58	**36.2**	1.76 1.63, *m*	**36.1**	1.35, *m* 1.51,	**33.2**	1.26 1.38, *m*	**31.2**
8	-	**41.6**	-	**41.8**	-	**43.8**	-	**42.2**
9	1.68, *m*	**48.2**	1.75	**48.4**	1.81, *d* (8.6)	**52.4**	2.14, *br s*	**53.8**
10	-	**43.1**	-	**43.1**	-	**44.7**	-	**42.2**
11	2.11, *ddd* (19.3, 11.5, 2.9) 2.57, *dt* (19.3, 5.40)	**26.9**	2.56, *dt* (19.0, 5.2) 2.14, *ddd* (19.0, 11.5, 2.6)	**27.0**	4.11, *dd* (8.6, 3.3)	**75.6**	6.79, *dd* (10.6, 1.0)	**133.2**
12	5.43, *t* (3.2)	**128.6**	5.27, *t* (3.2)	**127.3**	5.42, *d* (3.3)	**122.8**	5.46, *dd* (10.6, 3.0)	**132.1**
13	-	**137.7**	-	**138.6**	-	**145.1**	-	**84.7**
14	-	**47.4**	-	**47.6**	-	**41.9**	-	**45.0**
15	4.27, *dd* (5.9, 11.4)	**67.1**	4.24, *dd* (11.7, 5.6)	**67.4**	1.08, *m* 1.71, *m*	**26.5**	1.81, *td* (12.5, 5.7) 1.00	**25.6**
16	1.88, *ddd* (12.3, 6.2, 1.2) 1.97, *t* (12.7)	**33.2**	1.90, *t* (12.7) 1.48, *dd* (13.2, 6.1)	**34.2**	1.98, *td* (13.9-5.1) 1.28, *m*	**23.1**	2.05, *td* (13.4, 4.5) 1.16, *dd* (13.6, 5.4)	**27.1**
17	-	**49.8**	-	**38.7**	-	**37.9**	-	**42.3**
18	1.97, *d* (10.8)	**52.6**	1.4	**54.0**	1.5	**53.5**	1.23, *d* (12.1)	**61.1**
19	1.43	**38.4**	1.41	**39.2**	1.32, *m*	**38.9**	1.73, *m*	**37.8**
20	0.99, *m*	**38.8**	0.92	**39.1**	0.97, *m*	**39.3**	0.90, *m*	**40.8**
21	1.59 129	**29.8**	1.51, *m* 1.24, *m*	**30.4**	1.28, *m* 153	**30.4**	1.31 1.51, *m*	**31.6**
22	1.44, *td* (14.1, 4.2) 1.27	**31.0**	1.40 1.58	**34.7**	1.34 1.61	**35.0**	1.33 1.59, *m*	**35.0**
23	0.99, *s*	**28.0**	1.00, *s*	**28.0**	1.02, *s*	**28.1**	0.98, *s*	**27.8**
24	0.79, *s*	**15.3**	0.81, *s*	**15.3**	0.82, *s*	**15.2**	0.79, *s*	**14.7**
25	1.00	**11.1**	1.04, *s*	**11.3**	1.09, *s*	**13.0**	1.00, *s*	**13.8**
26	0.87, *s*	**18.1**	1.10, *s*	**17.7**	1.06, *s*	**18.1**	1.13, *s*	**19.5**
27	1.13, *s*	**16.9**	1.15, *s*	**17.0**	1.21, *s*	**22.4**	1.08, *s*	**17.2**
28	9.27, *d* (1.1)	**206.6**	3.52, *d* (10.8) 3.25, *d* (11)	**70.3**	3.22, *d* (11.0) 3.51, *d* (11.0)	**69.7**	3.68, *d* (6.7) 3.23, *dd* (6.7, 1.5)	**76.7**
29	0.93, *d* (6.5)	**16.6**	0.88, *d* (5.2)	**17.4**	0.93, *d* (6.4)	**17.5**	1.02, *d* (6.2)	**19.5**
30	0.99	**21.0**	0.97, *d* (5.6)	**21.3**	0.99, *d* (6.6)	**21.3**	0.95, *d* (6.1)	**18.2**
O-CH_3	-	**-**	-		3.4, *s*	**54.0**	-	**-**

[a] overlapped ^{1}H NMR signals are reported without designated multiplicity.

Table 3

^{1}H and ^{13}C NMR spectroscopic data of compounds 9 in $CDCl_3$; 10 and 11 in CD_3OD

Position	9		10		11	
	δ_H (*J* in Hz)	δ_c	δ_H (*J* in Hz)	δ_c	δ_H (*J* in Hz)	δ_c
1	0.99 1.7, *dt* (12.5, 3.3)	**38.5**	0.97 1.68	**39.9**	2.69, *dd* (20.4, 9.9)	**44.3**
2	1.65 1.61	**27.2**	1.65 1.61, *m*	**27.9**	1.78 1.19	**33.4**
3	3.26, *dd* (11.5, 4.6)	**78.7**	3.19, *dd* (11.0, 4.8)	**79.4**	3.62, *dd* (11.4, 6.0)	**79.7**
4	-	**38.2**	-	**39.6**	-	**43.8**
5	0.84	**52.1**	0.86, *dd* (14.7, 1.9)	**53.6**	1.74	**51.3**
6	1.57 1.77, *dd* (12.5, 4.3)	**28.0**	1.58 1.78, *dd* (12.7, 3.9)	**28.6**	1.47, *m* 1.40, *m*	**21.7**
7	3.94, *dd* (11.2, 4.9)	**72.0**	3.9, *dd* (11.3, 4.8)	**73.0**	1.75 1.63, *m*	**36.3**
8	-	**46.5**	-	**47.6**	-	**44.9**
9	1.41, *brd* (9.0)	**48.2**	1.46	**49.2**	2.35, *d* (10.0)	**53.8**
10	-	**37.2**	-	**38.3**		**59.7**
11	2.03 2.00	**23.4**	1.96 2.2	**24.7**	3.72, *br d* (9.20)	**67.3**
12	5.32, *t* (3.3)	**126.9**	5.39, *br s*	**125.6**	5.17 br *s*	**128.1**
13	-	**138.9**	-	**146.0**	-	**143.3**
14	-	**49.0**	-	**49.8**	-	**43.8**
15	4.24, *dd* (11.8, 5.4)	**66.0**	4.21, *dd* (11.9, 5.1)	**67.0**	1.85, *m* 1.22, *m*	**27.8**
16	1.51, *dd* (13.1, 3.8) 1.94, t (12.5)	**32.6**	1.94(t, 12.4) 1.46	**31.9**	1.98, *m* 1.31	**24.3**
17	-	**38.2**	-	**38.6**	-	**39.0**
18	1.39, d (10.7)	**55.5**	2.07, *dd* (14.2, 4.5)	**45.0**	1.48, *m*	**55.4**
19	1.45, *m*	**39.3**	1.1, *m* 1.81, *t* (13.4) 1.1 m	**47.4**	1.48, *m*	**40.8**
20	0.91, *m*	**39.3**	-	**31.8**	0.95	**40.6**
21	1.24, *m* 1.50, *dm* (13.3)	**30.4**	1.21 1.36, *m*	**35.2**	1.50 1.31	**31.7**
22	1.67 1.35, *td* (13.2, 3.9)	**34.7**	1.57 1.4	**31.8**	1.60, *m* 1.41, *m*	**36.2**
23	1.02, *s*	**28.1**	1.03, *s*	**28.7**	1.00, *s*	**27.3**
24	0.83, *s*	**15.7**	0.83, *s*	**16.4**	0.71, *s*	**16.5**
25	0.98, *s*	**15.7**	0.99, *s*	**16.0**	3.32 3.07, *b rs*	**48.9**
26	1.06, *s*	**10.0**	1.03, *s*	**10.7**	1.08, *s*	**17.3**
27	1.18, *s*	**16.5**	1.22, *s*	**20.2**	1.27	**23.3**
28	3.15, *d* (11.2) 3.58, *d* (11.2)	**70.5**	3.47, *d* (11.0) 3.18, *d* (11.0)	**70.1**	3.51, *d* (11.2) 3.08, *d* (11.1)	**70.0**
29	0.84, *d* (6.3)	**17.3**	0.92, *s*	**33.7**	0.94	**17.4**
30	0.96, *d* (6.1)	**21.2**	0.91, *s*	**23.9**	0.98	**21.7**

[a] overlapped ^{1}H NMR signals are reported without designated multiplicity.

Supplementary material

Triterpenoids from *Salvia argentea* var. *aurasiaca* (Pomel) Batt. & Trab. and their chemotaxonomic significance

Hichem Lakhal[a,b], Ahmed Kabouche[a], Abdulmagid Alabdul Magid[c], Laurence Voutquenne-Nazabadioko[c], Dominique Harakat[d], Zahia Kabouche[a*]

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[b] Centre de Recherche en Biotechnologies (CRBt), B.P. 73 UV 01, Ali Mendjeli -Nouvelle ville, 25000 Constantine, Algérie
[c] Groupe Isolement et Structure, Institut de Chimie Moléculaire de Reims (ICMR), CNRS UMR 7312, UFR de Pharmacie, BP 1039, 51687 Reims, France.
[d] Service Commun d'Analyses, Institut de Chimie Moléculaire de Reims (ICMR), CNRS UMR 7312, Bat. 18 B.P.1039, 51687 Reims Cedex 2, France

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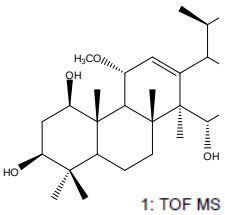
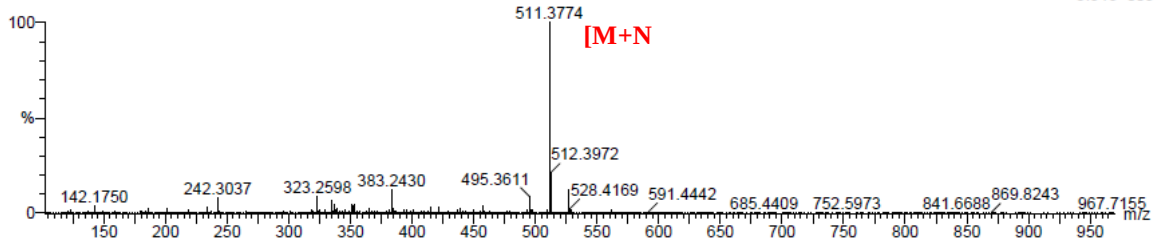
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1471 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 31-31 H: 0-1000 N: 0-5 O: 0-15 23Na: 0-1 56Fe: 0-1 90Zr: 0-1 I: 0-1



Hichem 1
13HR137 86 (5.976) AM (Top,4, Ar,5000.0,472.69,1.00,LS 10); Sm (Mn, 2x1.00); Sb (1,40.00); Cm (86:107)

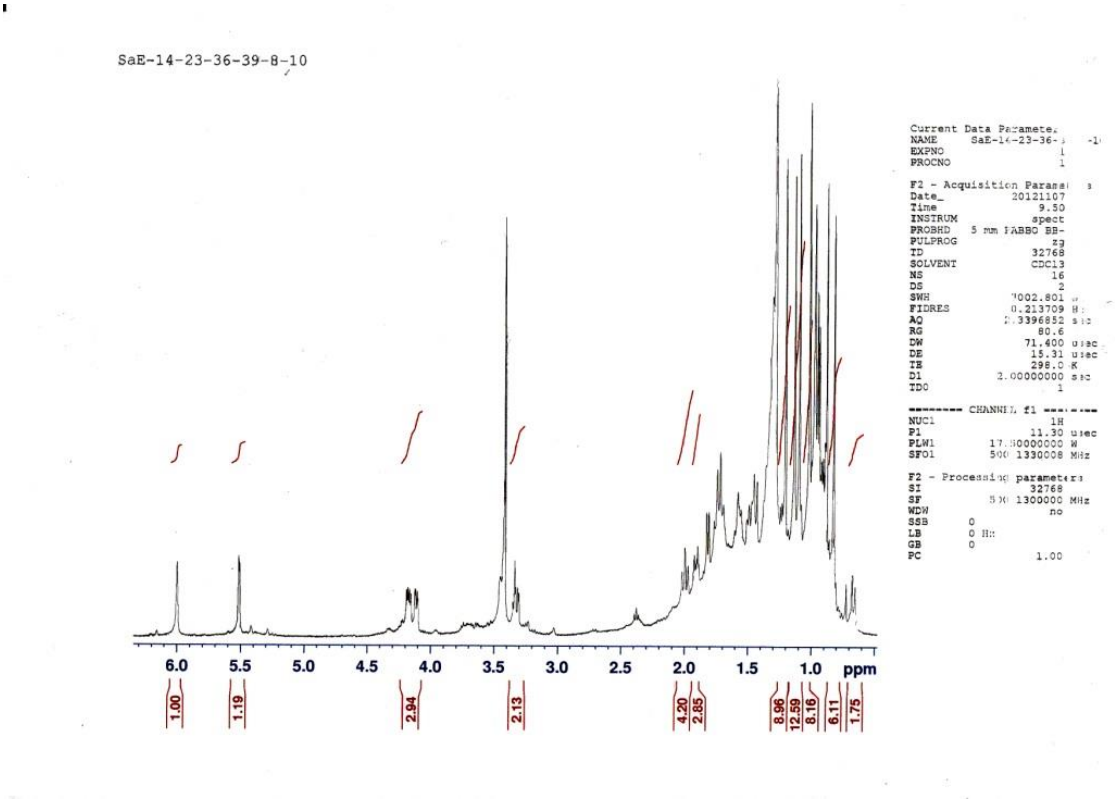
1: TOF MS ES+
3.54e+003



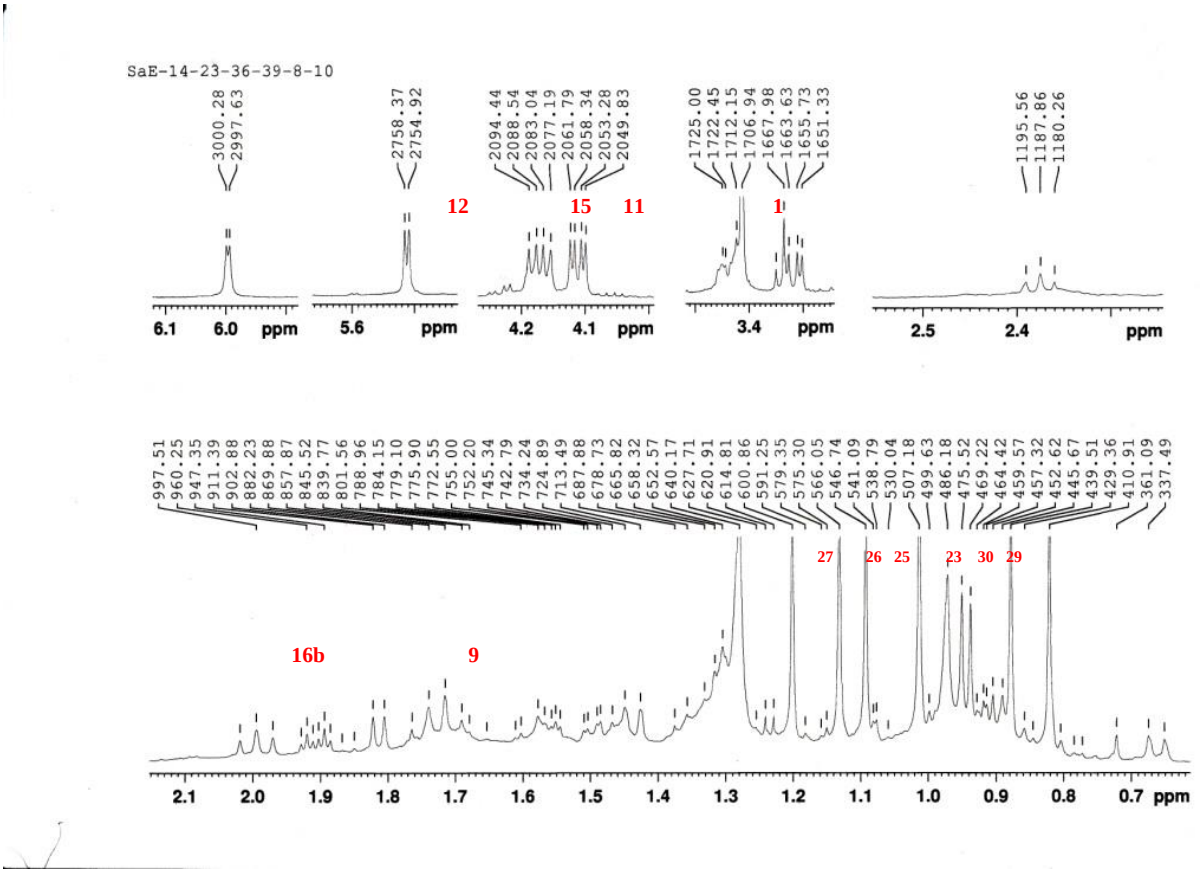
Minimum:				-1.5		
Maximum:		5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
511.3774	511.3763	1.1	2.2	5.5	111.5	C31 H52 O4 23Na

S1: HRESI-MS Spectrum of Compound **1**

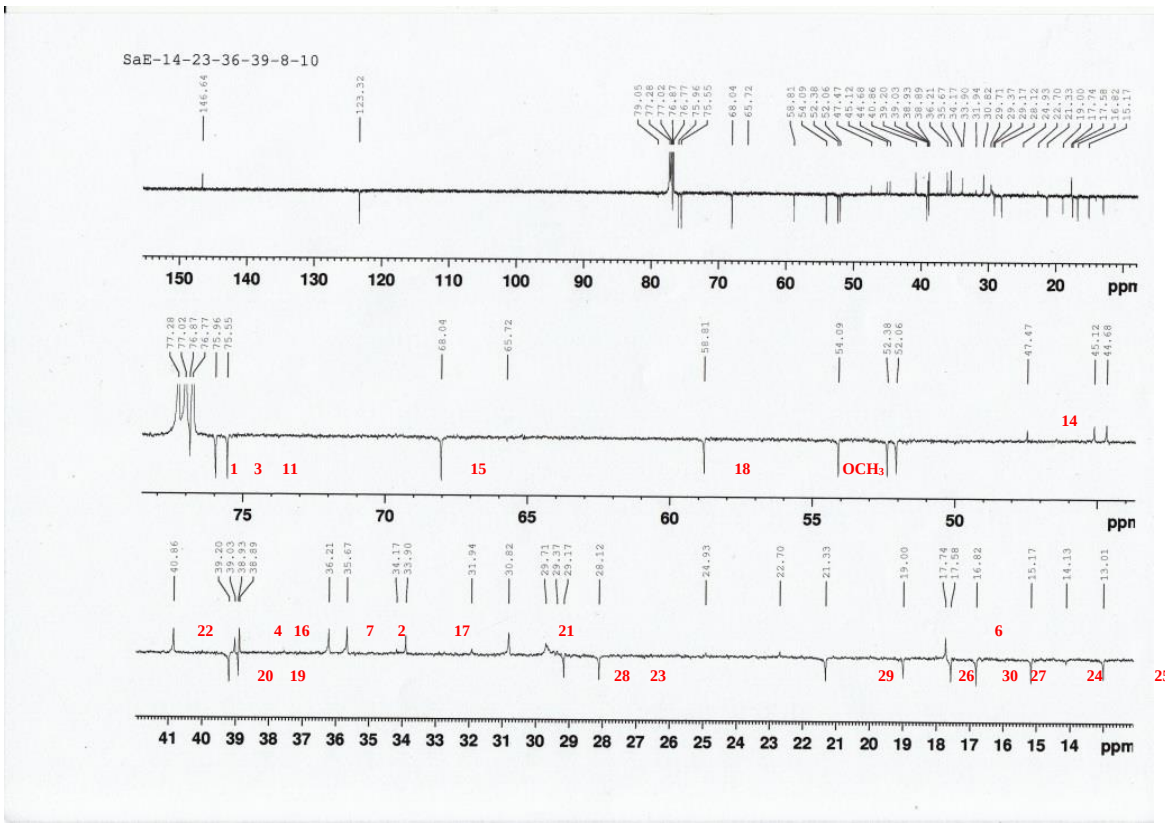
(11α-Methoxyurs-12-ene-1β, 3β, 15α-triol)



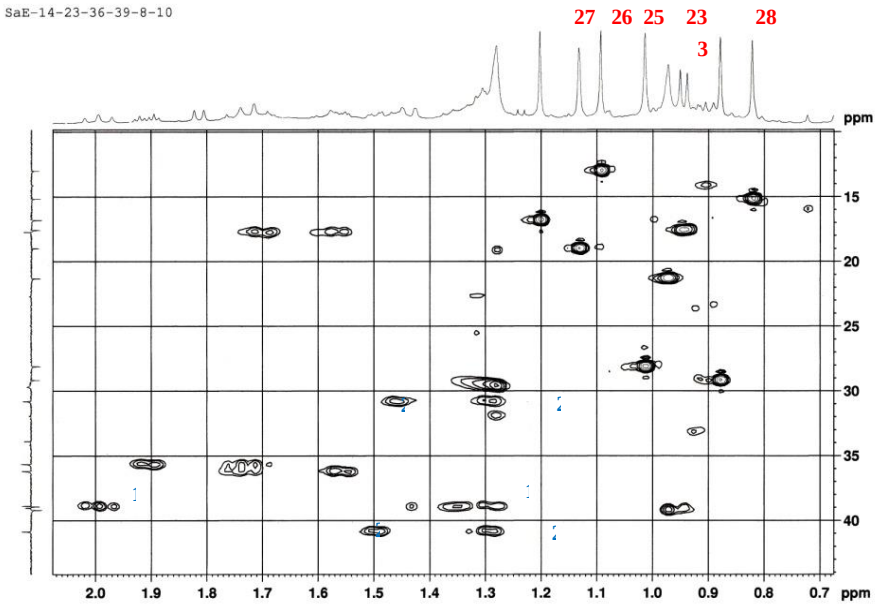
S2: ^{1}H-NMR (500 MHz, $CDCl_3$) Spectrum of Compound **1**



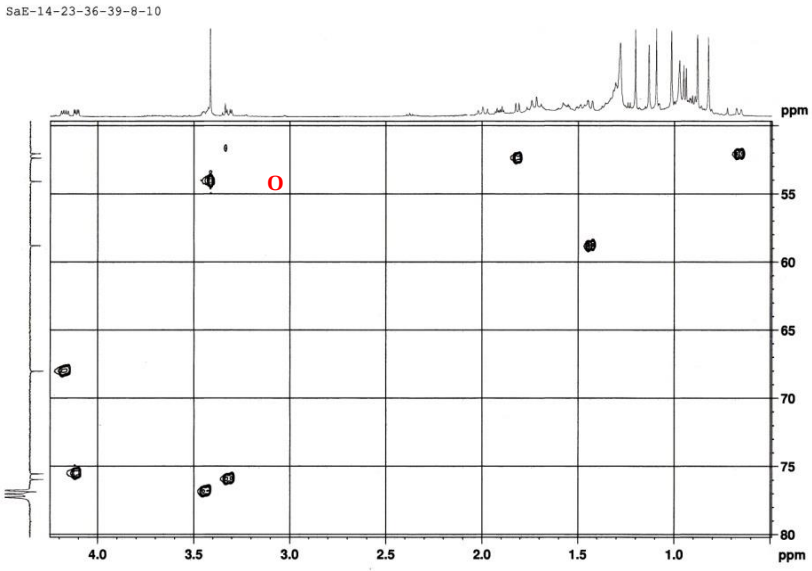
S3:[1]H-NMR Spectrum of Compound **1**



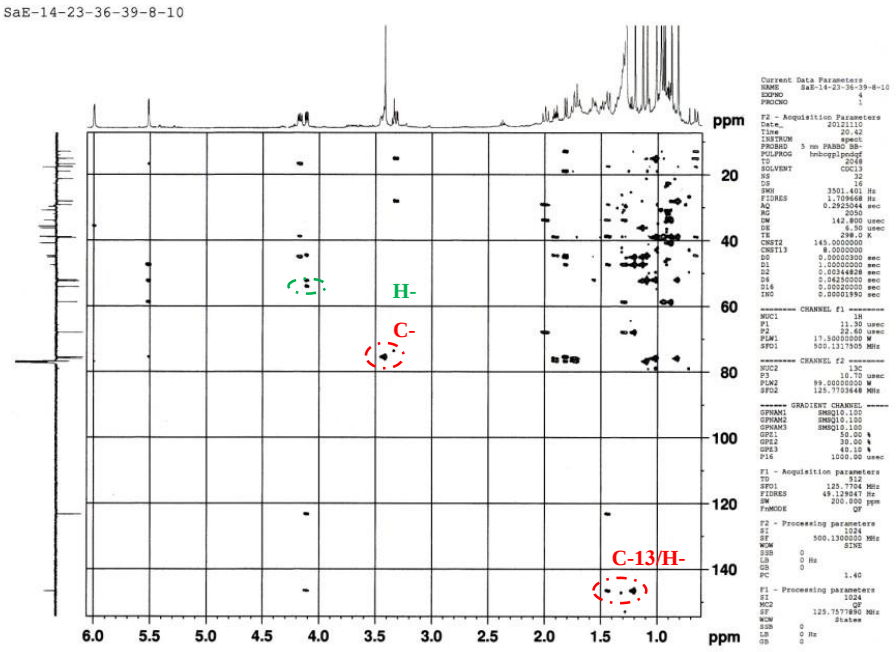
S4: [13]C-NMR J- mode (125 MHz, $CDCl_3$) Spectrum of Compound **1**



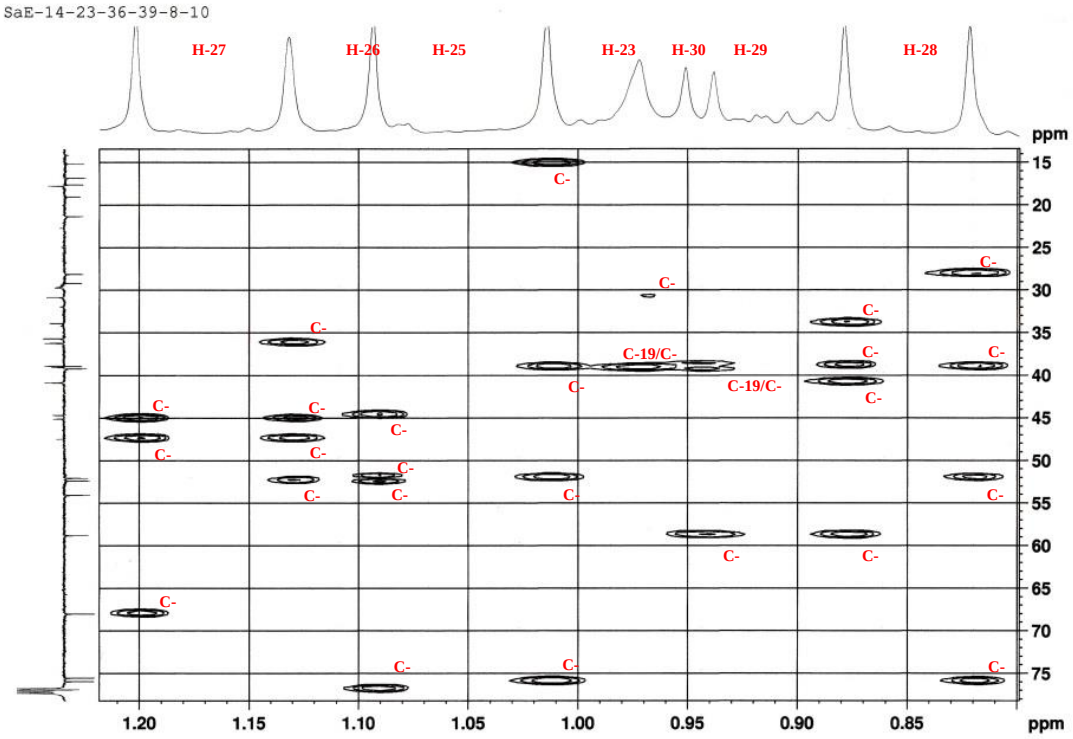
S5: HMQC (500 MHz) Spectrum of Compound **1** (From 10 to 45 ppm)



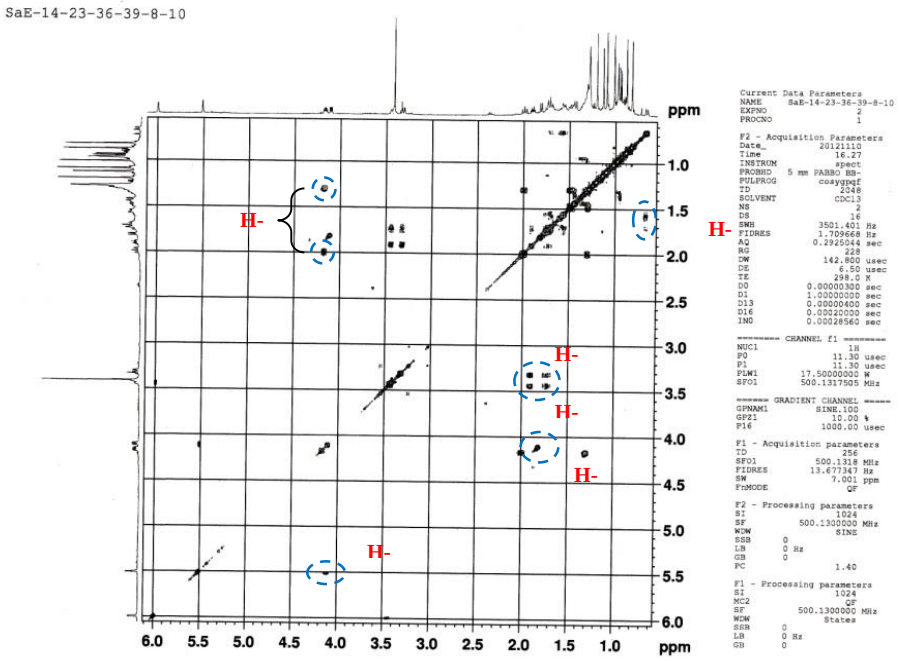
S6: HMQC (500 MHz) Spectrum of Compound **1** (From 50 to 80 ppm)



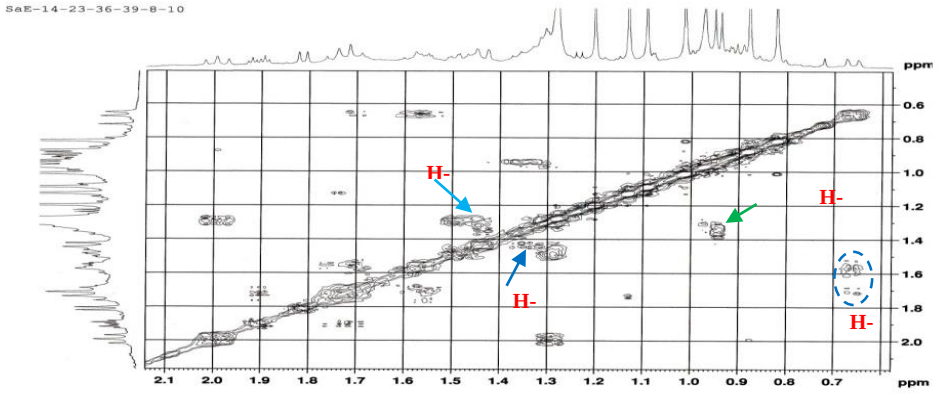
S7: HMBC (500 MHz) Spectrum of Compound **1**



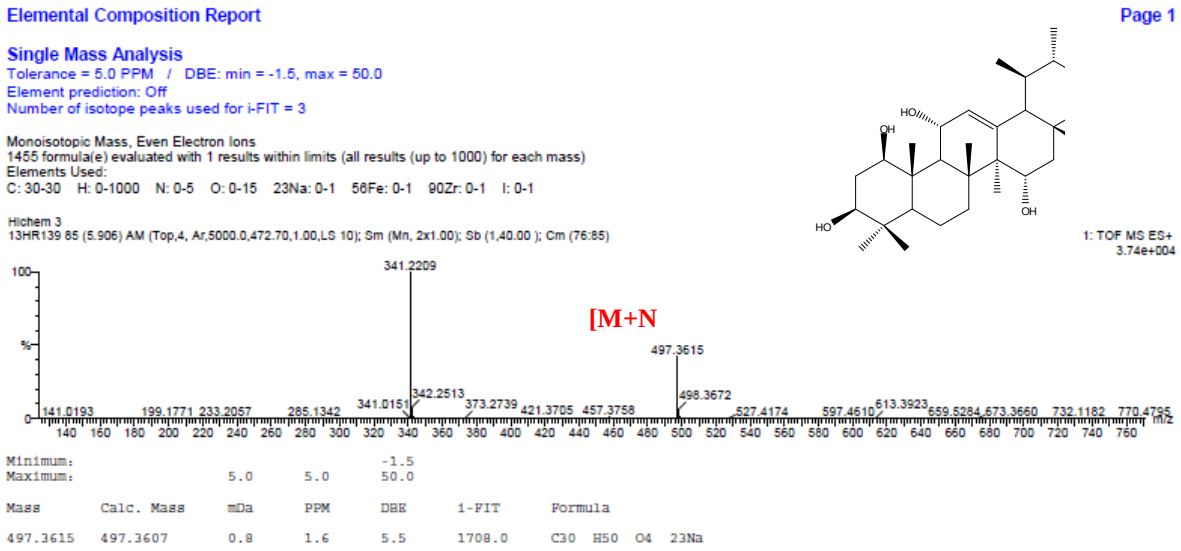
S8: HMBC (500 MHz) Spectrum of Compound **1** (From 12 to 78 ppm)



S9: COSY (500 MHz) Spectrum of Compound **1**

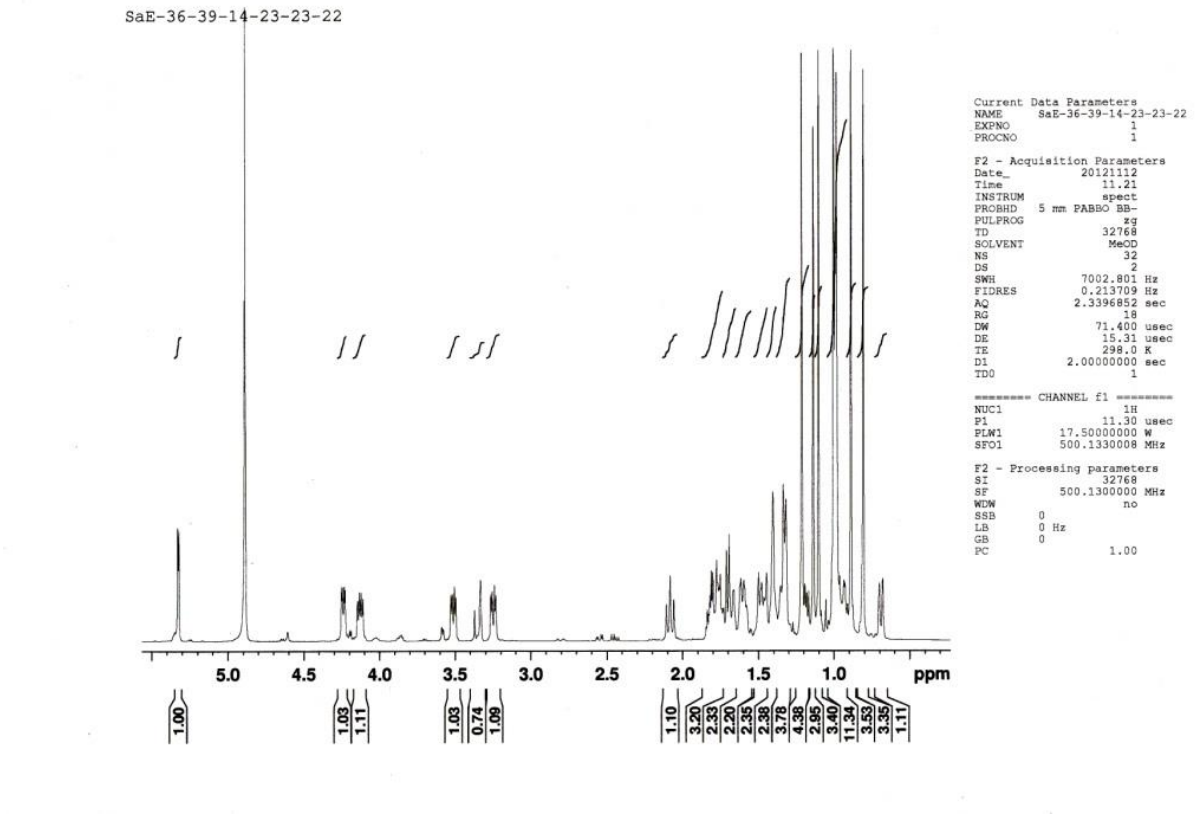


S10: COSY (500 MHz) Spectrum of Compound **1** (From 0.6 to 2.1 ppm)

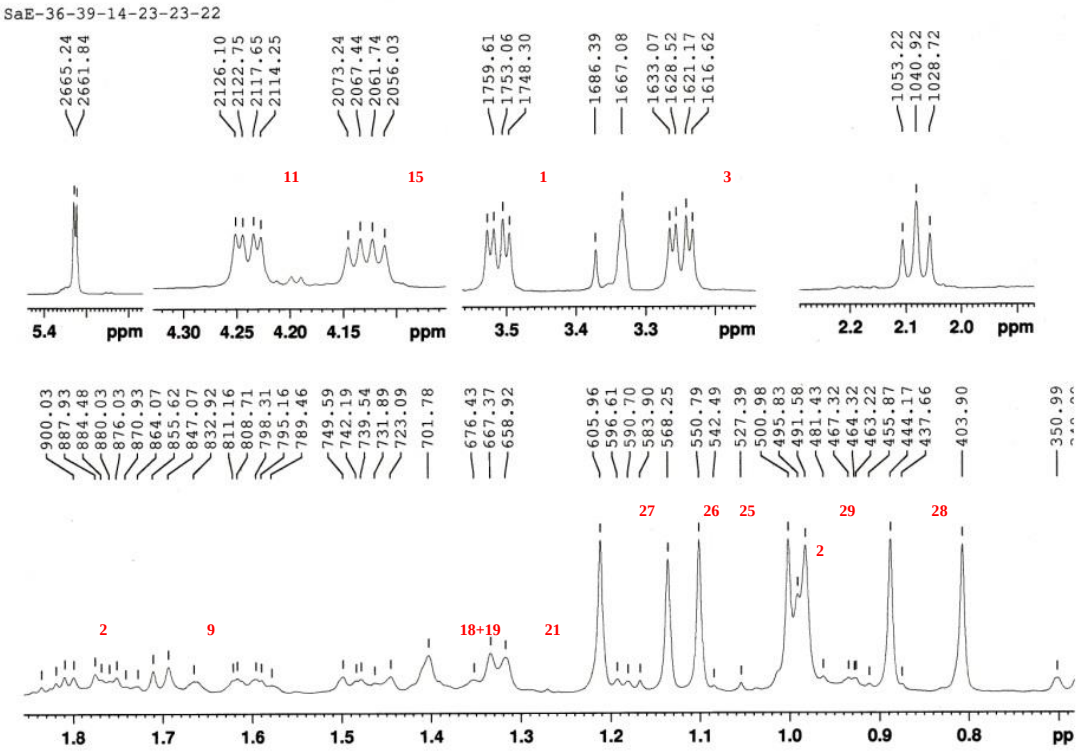


S11: HRESI-MS Spectrum of Compound **2**

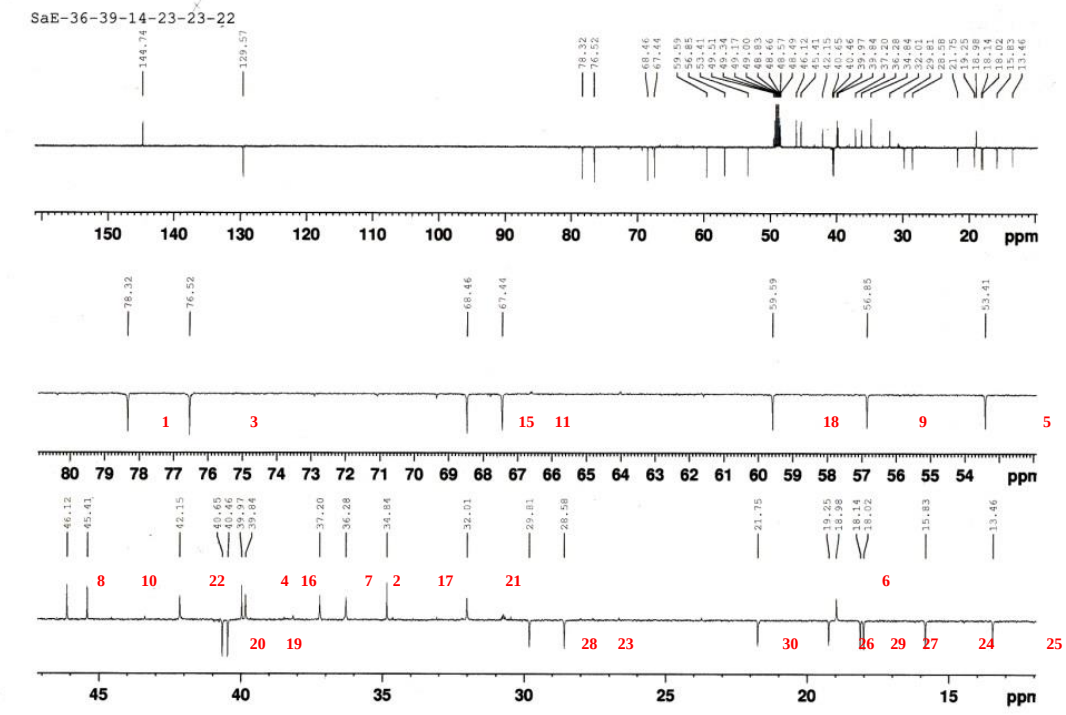
(Urs-12-ene-1β, 3β, 11α, 15α-tetraol)



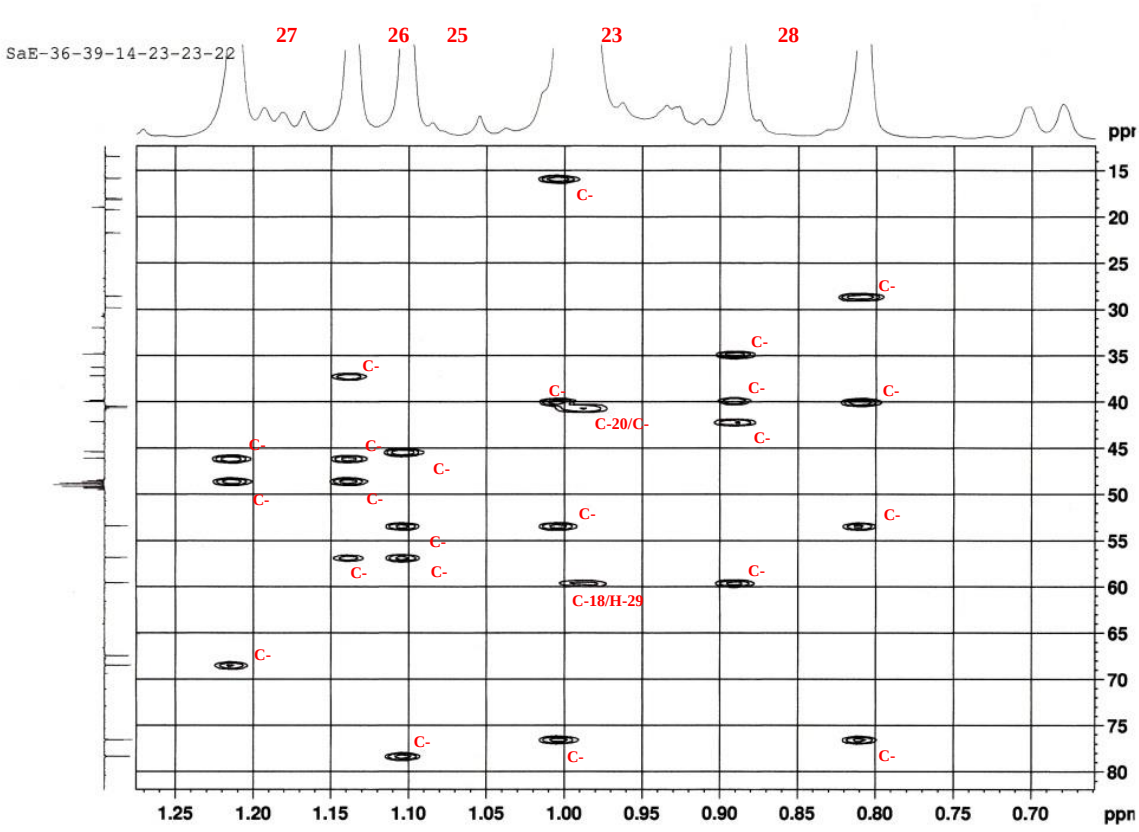
S12: ^{1}H-NMR (500 MHz, CD_3OD) Spectrum of Compound **2**



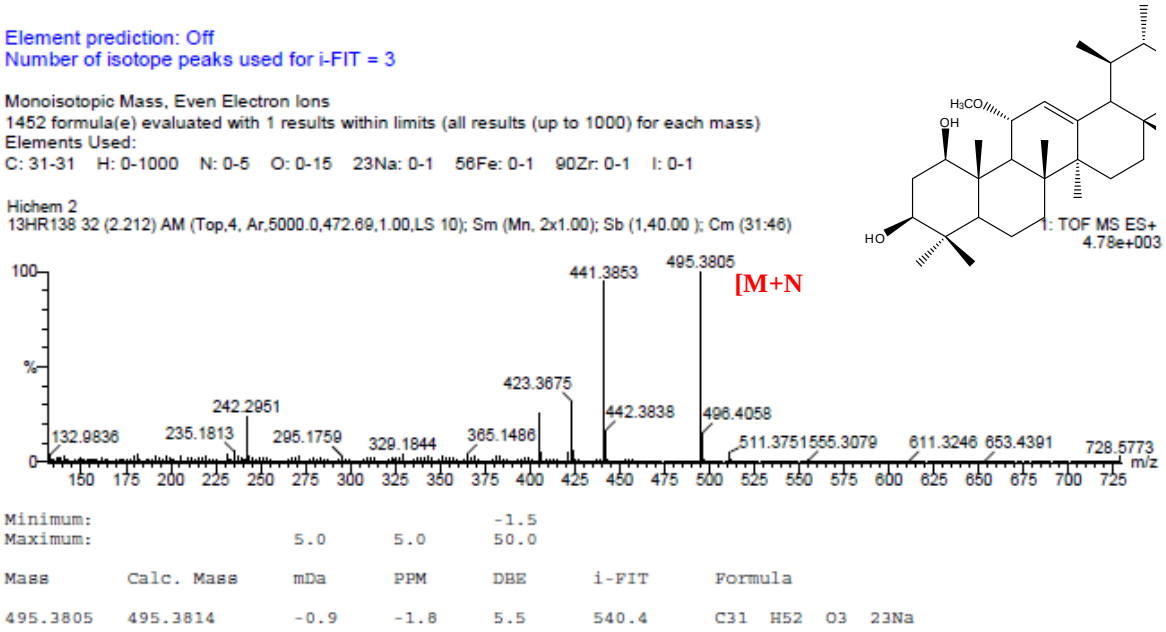
S13:1H-NMR (500 MHz, CD_3OD) Spectrum of Compound **2**



S14: ^{13}C-NMR J- mode (125 MHz, CD_3OD) Spectrum of Compound **2**

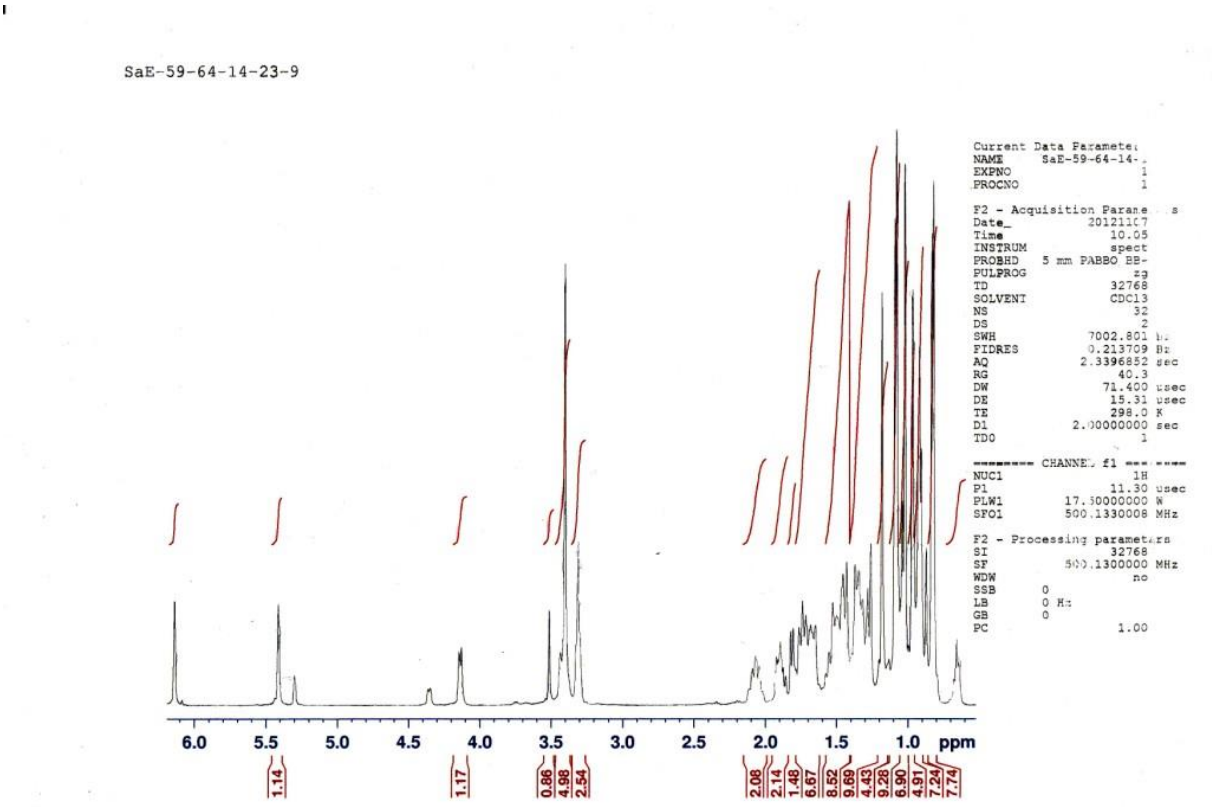


S15: HMBC (500 MHz) Spectrum of Compound **2** (From 12 to 82 ppm)

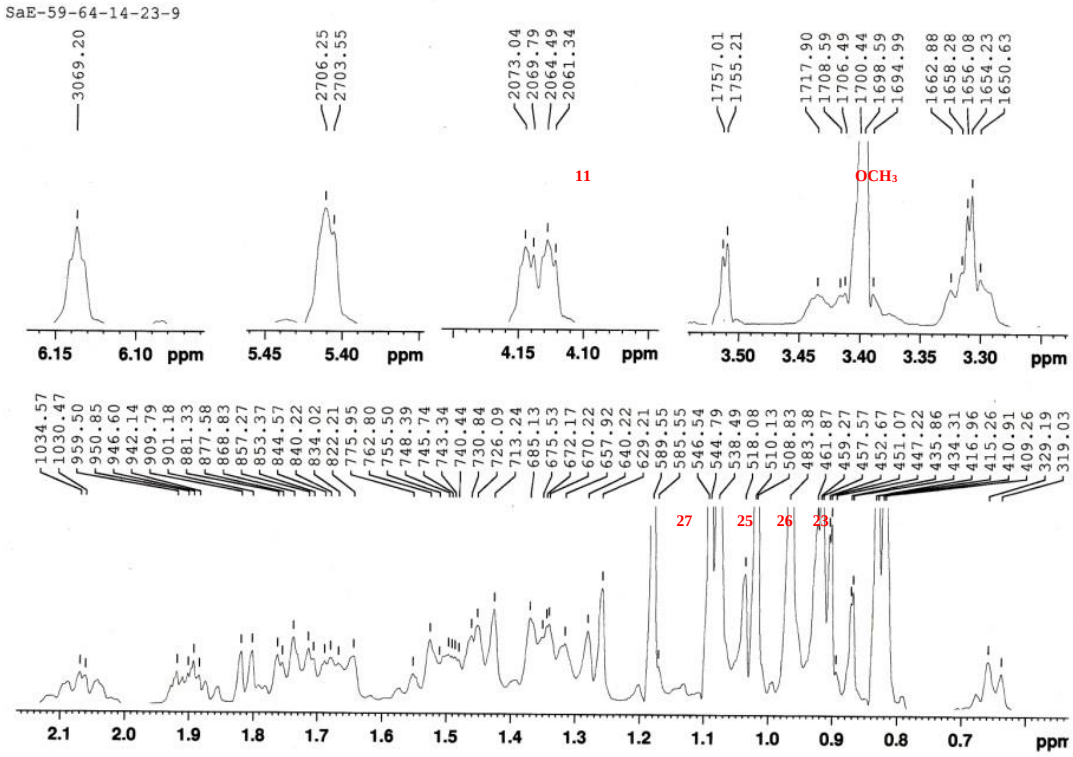


S16: HRESI-MS Spectrum of Compound **3**

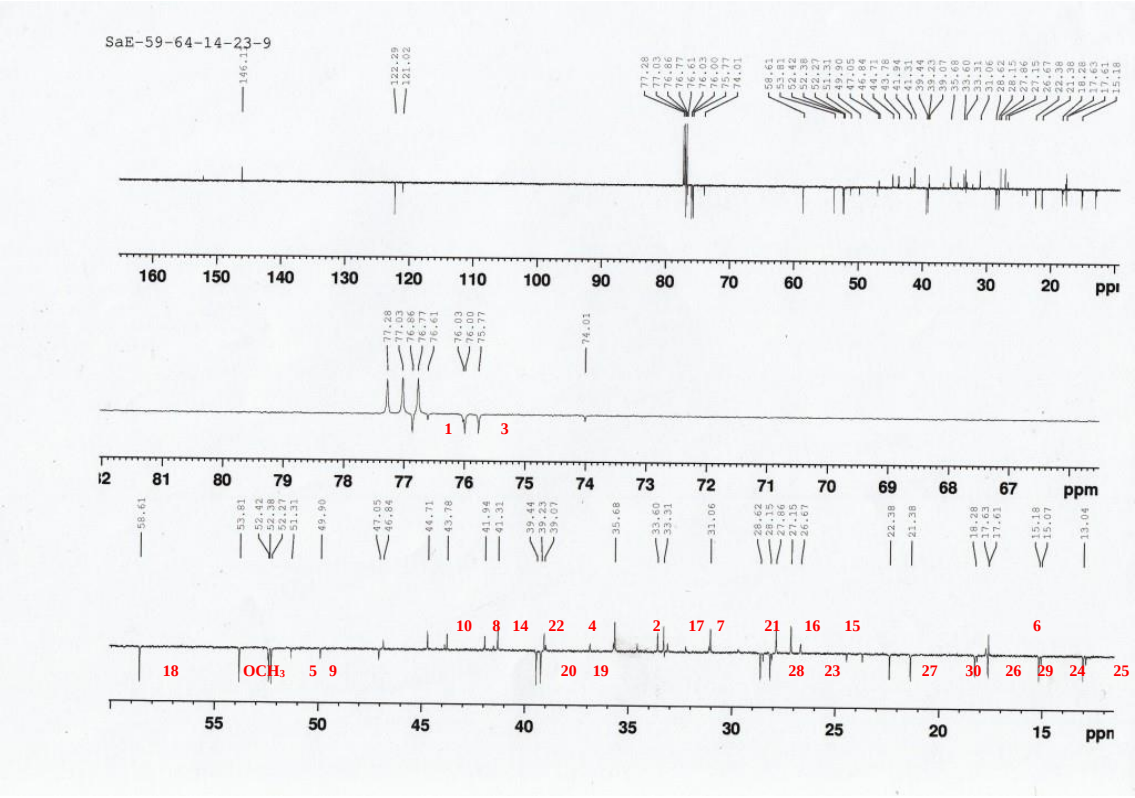
(11 α-methoxyurs-12-ene 1β,3β diol)



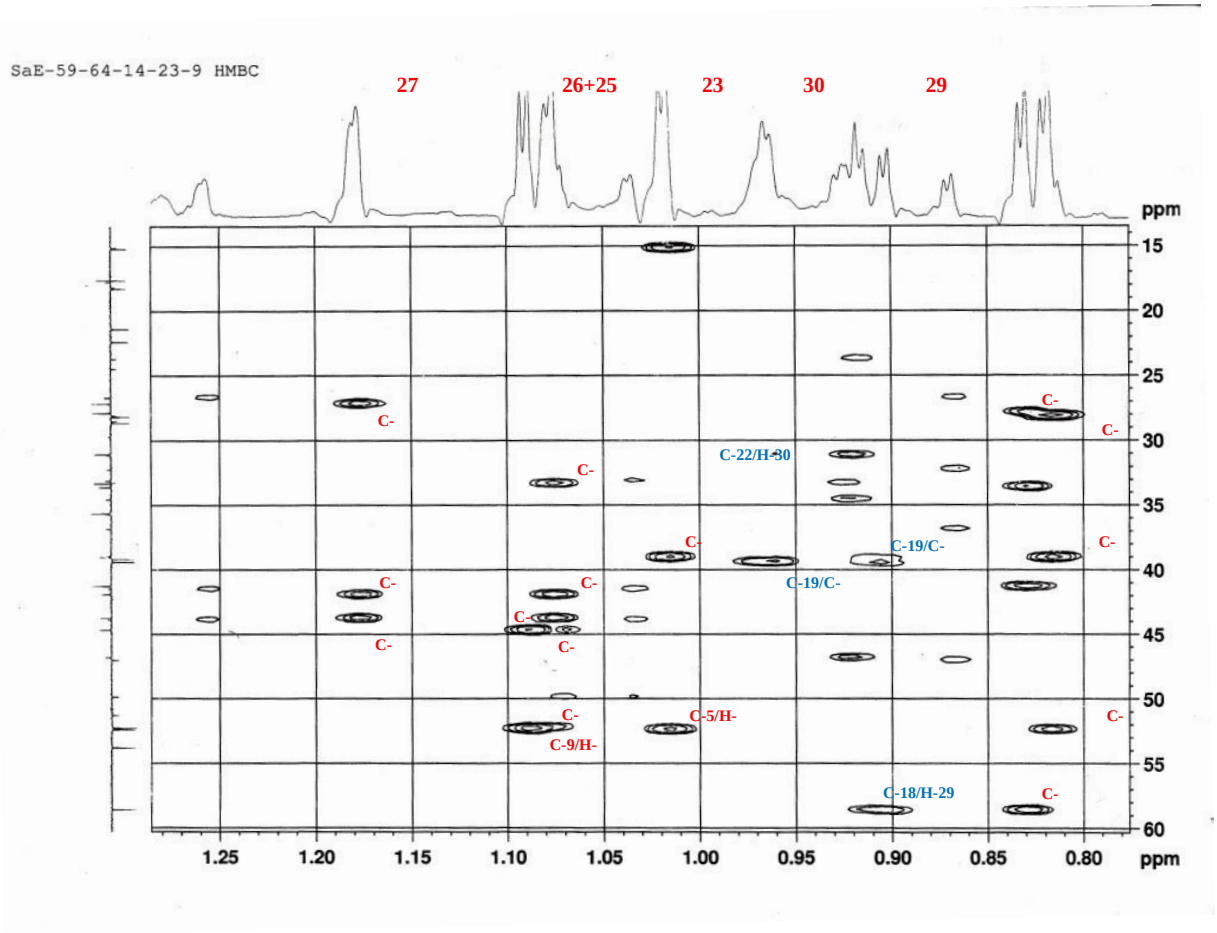
S17: ^{1}H-NMR (500 MHz, $CDCl_3$) Spectrum of Compound **3**



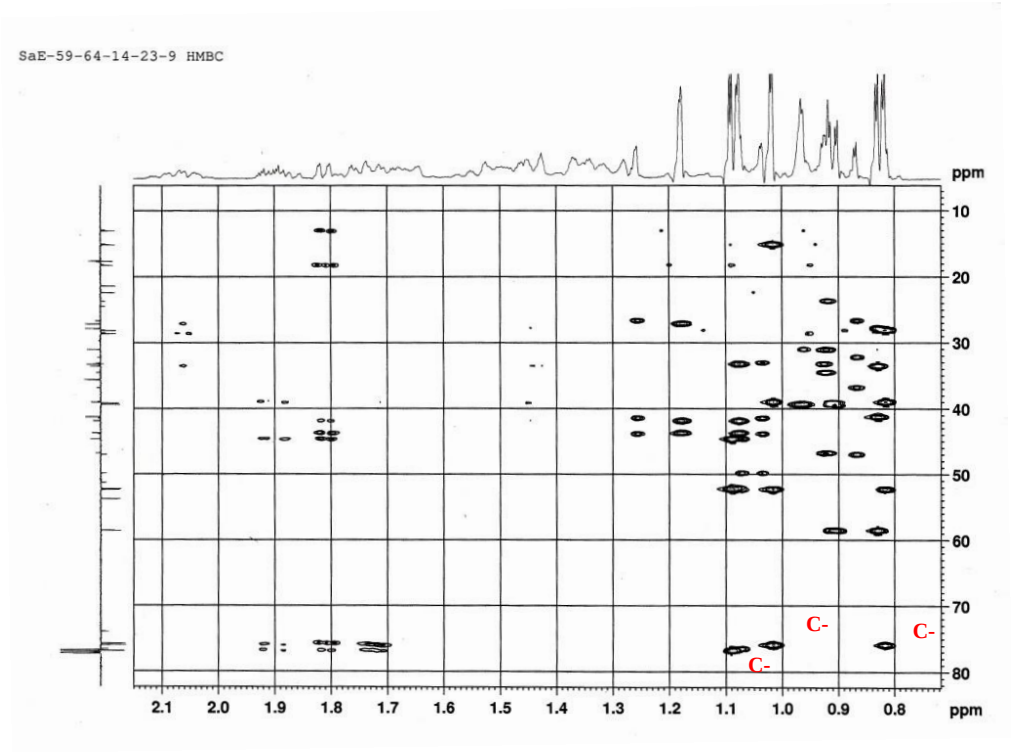
S18:[1]H-NMR (500 MHz, CDCl3) Spectrum of Compound **3**



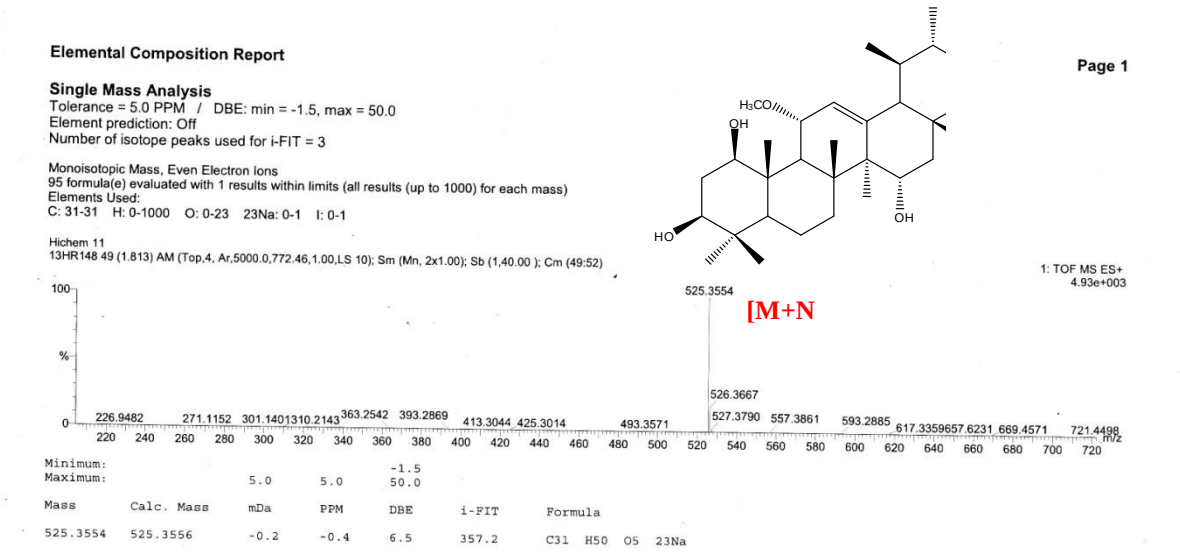
S19: [13]C-NMR J- mode (125 MHz, $CDCl_3$) Spectrum of Compound **3**



S20: HMBC (500 MHz) Spectrum of Compound **3** (From 13 to 60 ppm)

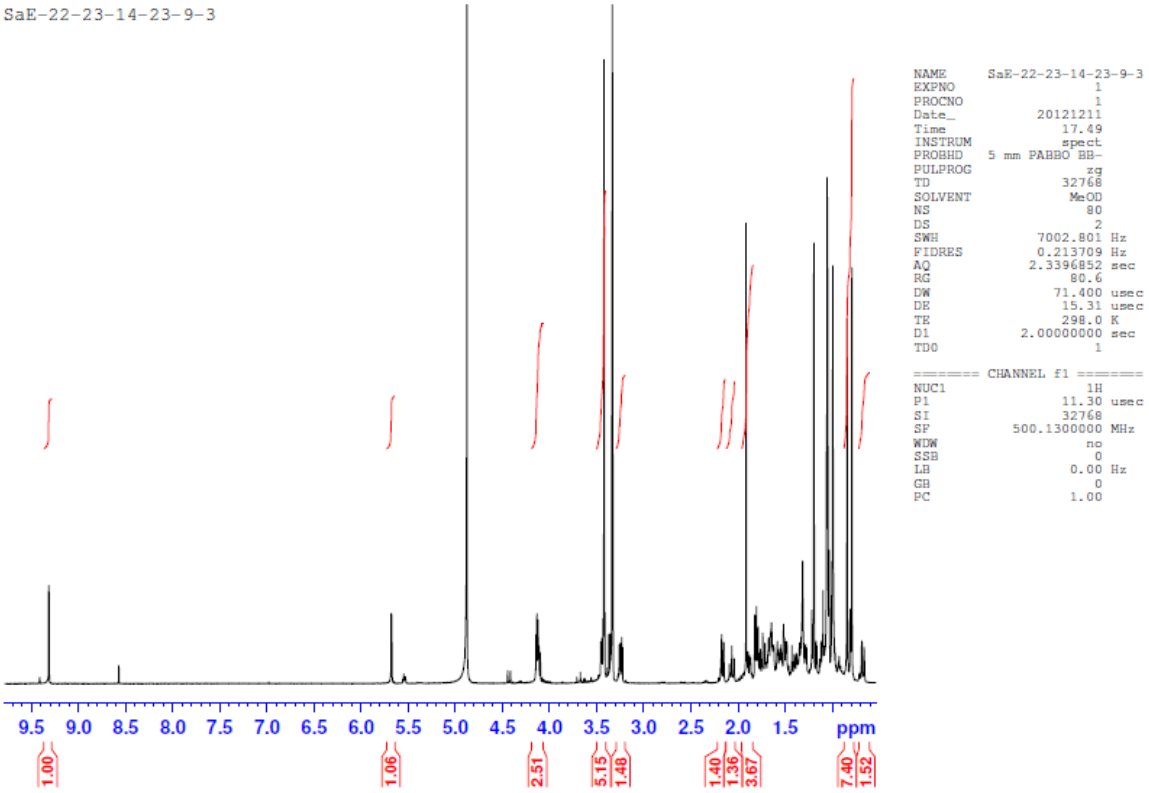


S21: HMBC (500 MHz) Spectrum of Compound **3** (From 10 to 80 ppm)

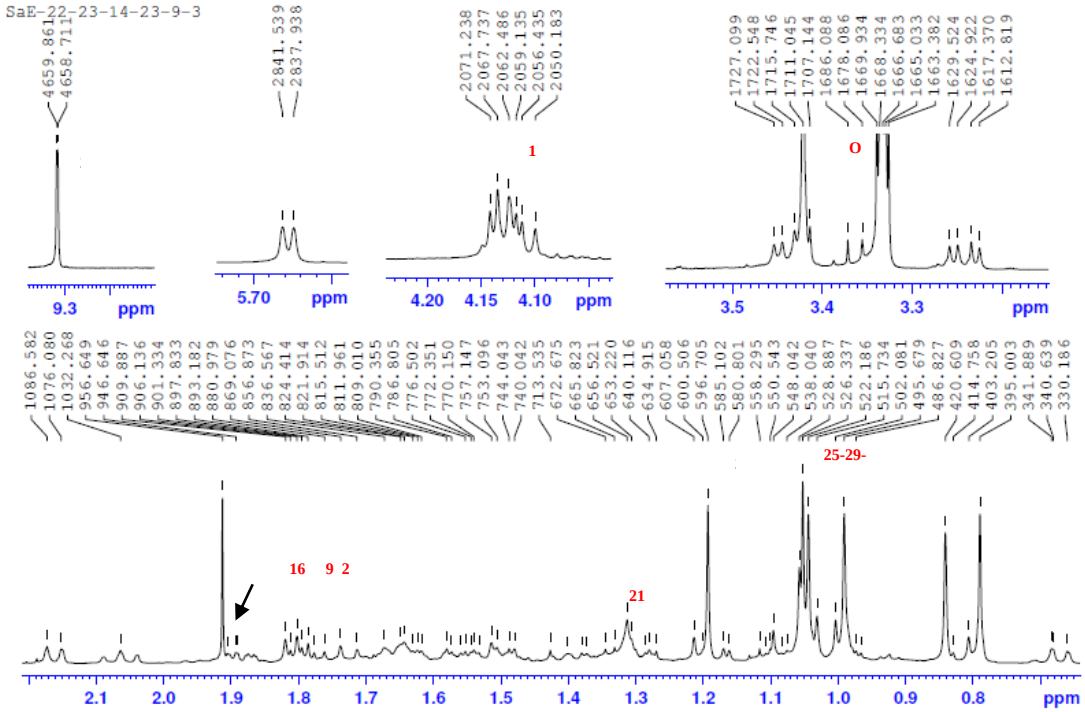


S22: HRESI-MS Spectrum of Compound **4**

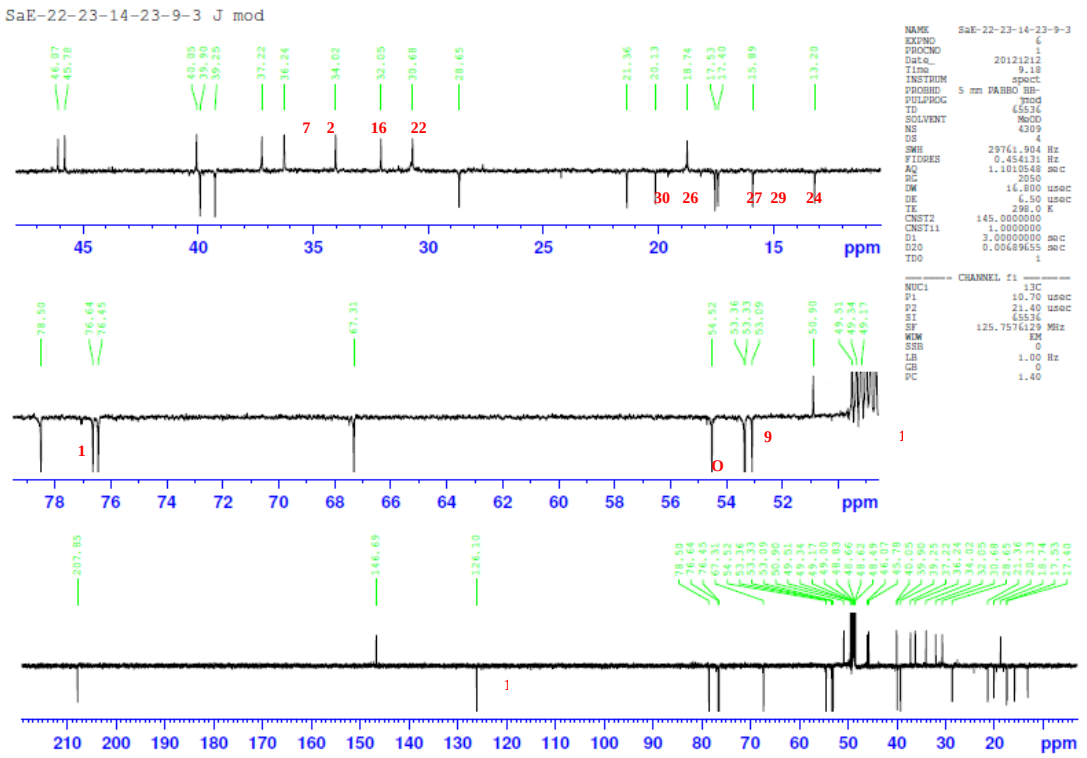
(1β, 3β, 15α trihydroxy-11α-methoxyurs-12-en-28-al)



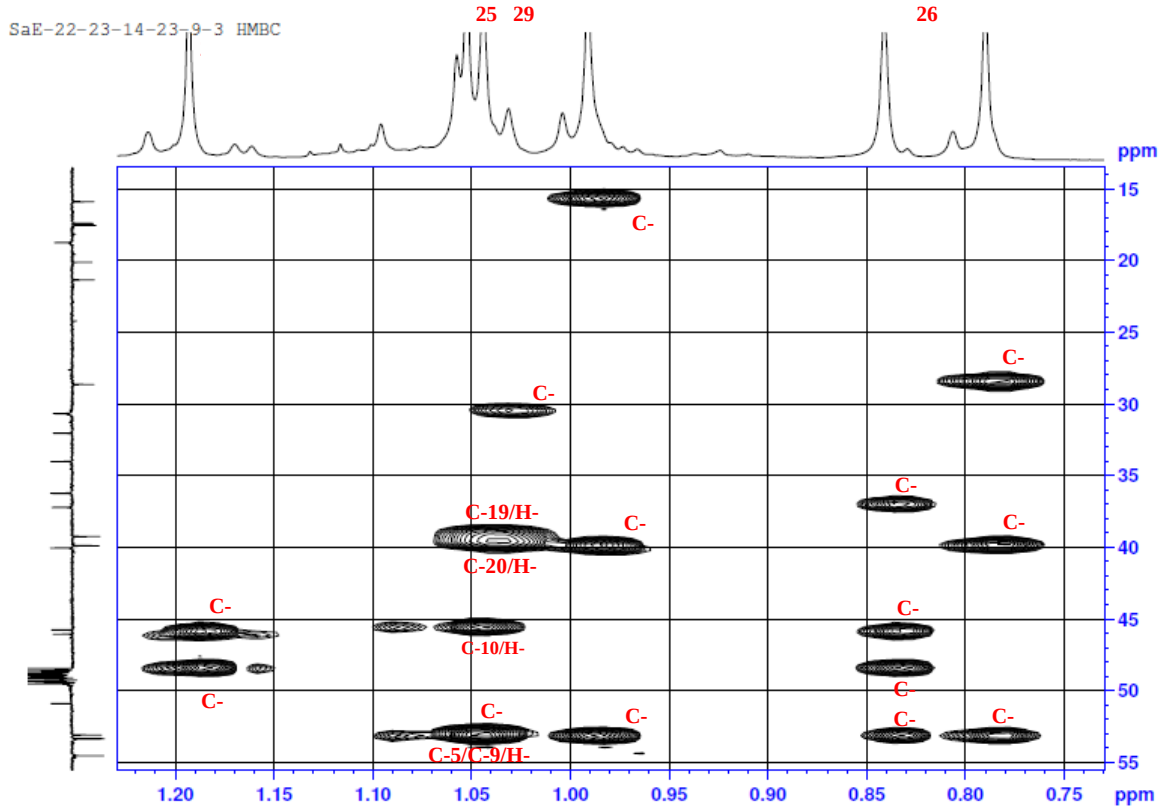
S23: ^{1}H-NMR (500 MHz, CD_3OD) Spectrum of Compound **4**



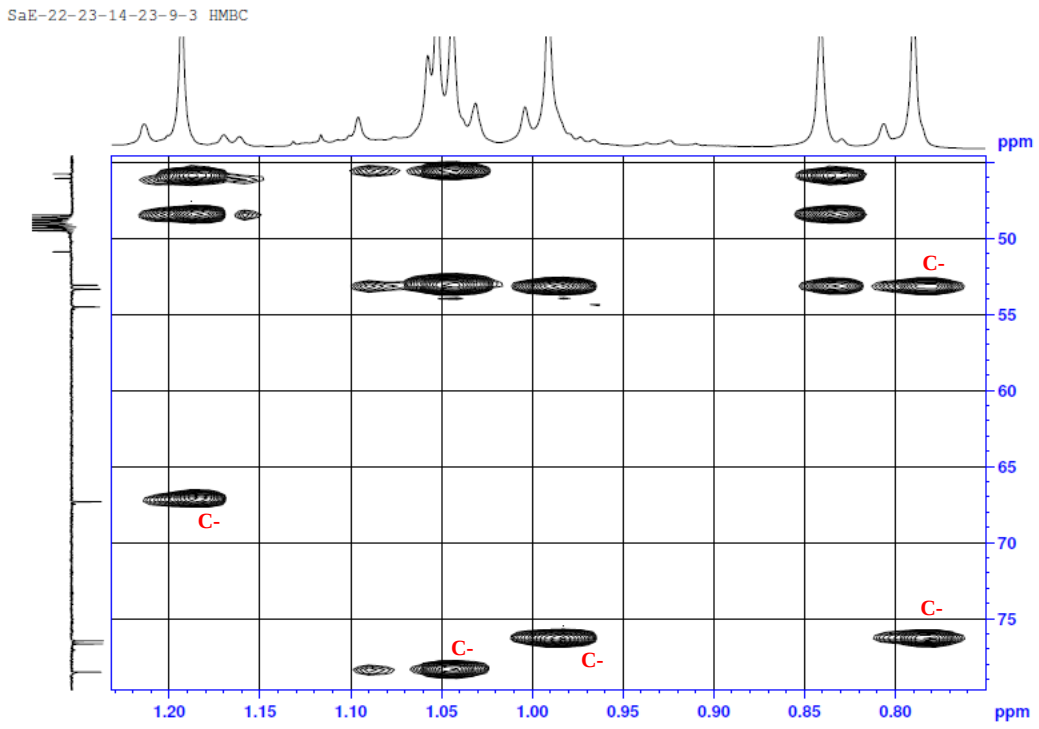
S24: ^{1}H-NMR (500 MHz, CD_3OD) Spectrum of Compound **4**



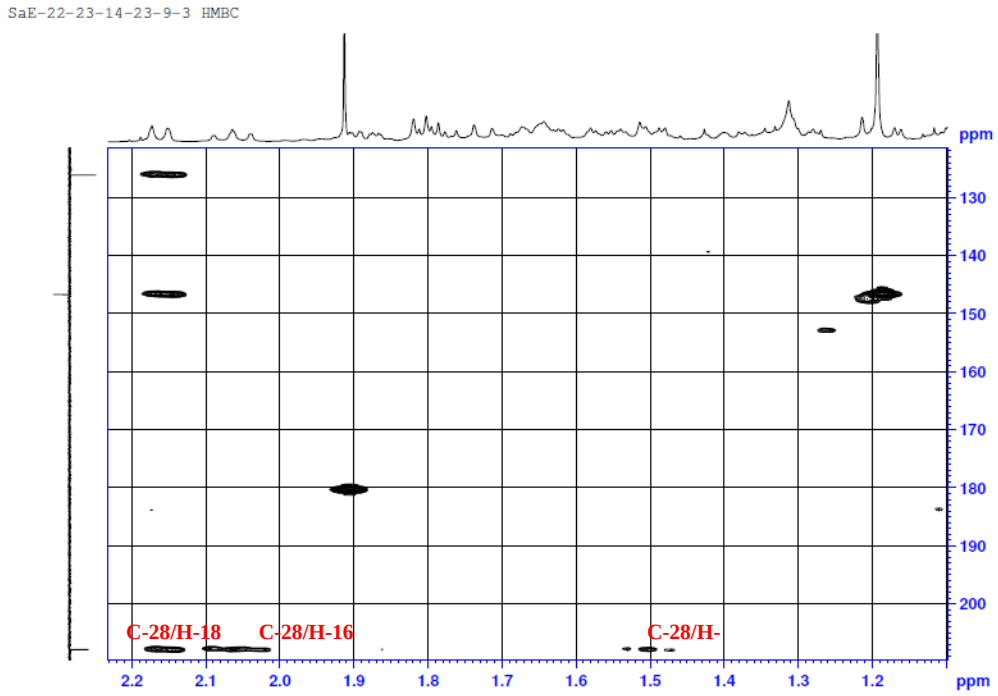
S25: ^{13}C-NMR J- mode (125 MHz, CD_3OD) Spectrum of Compound **4**



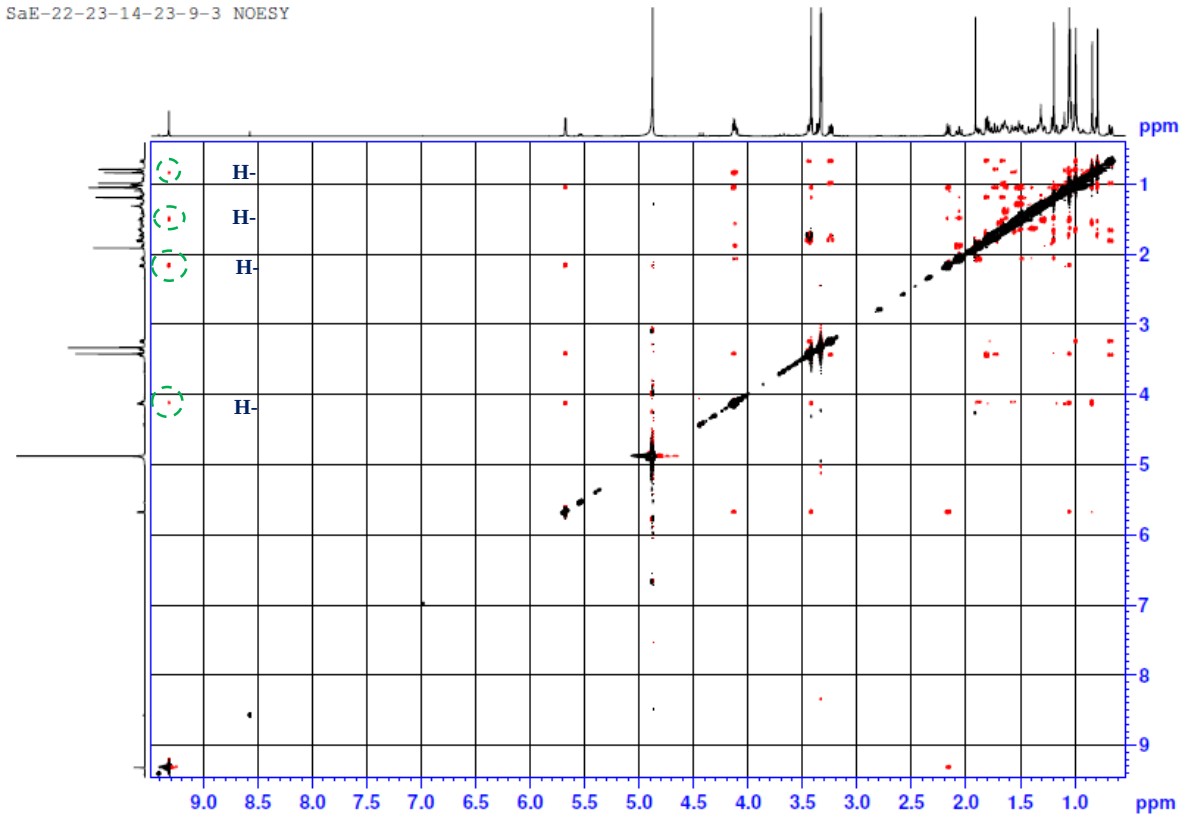
S26: HMBC (500 MHz) Spectrum of Compound **4** (From 14 to 55 ppm)



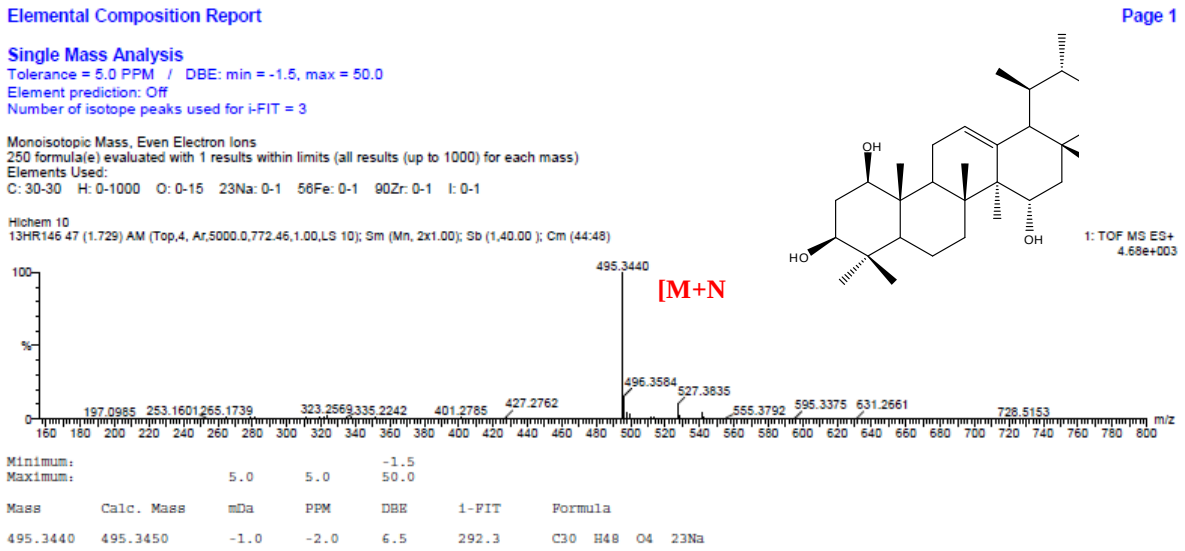
S27: HMBC (500 MHz) Spectrum of Compound **4** (From 45 to 80 ppm)



S28: HMBC (500 MHz) Spectrum of Compound **4** (From 120 to 210 ppm)

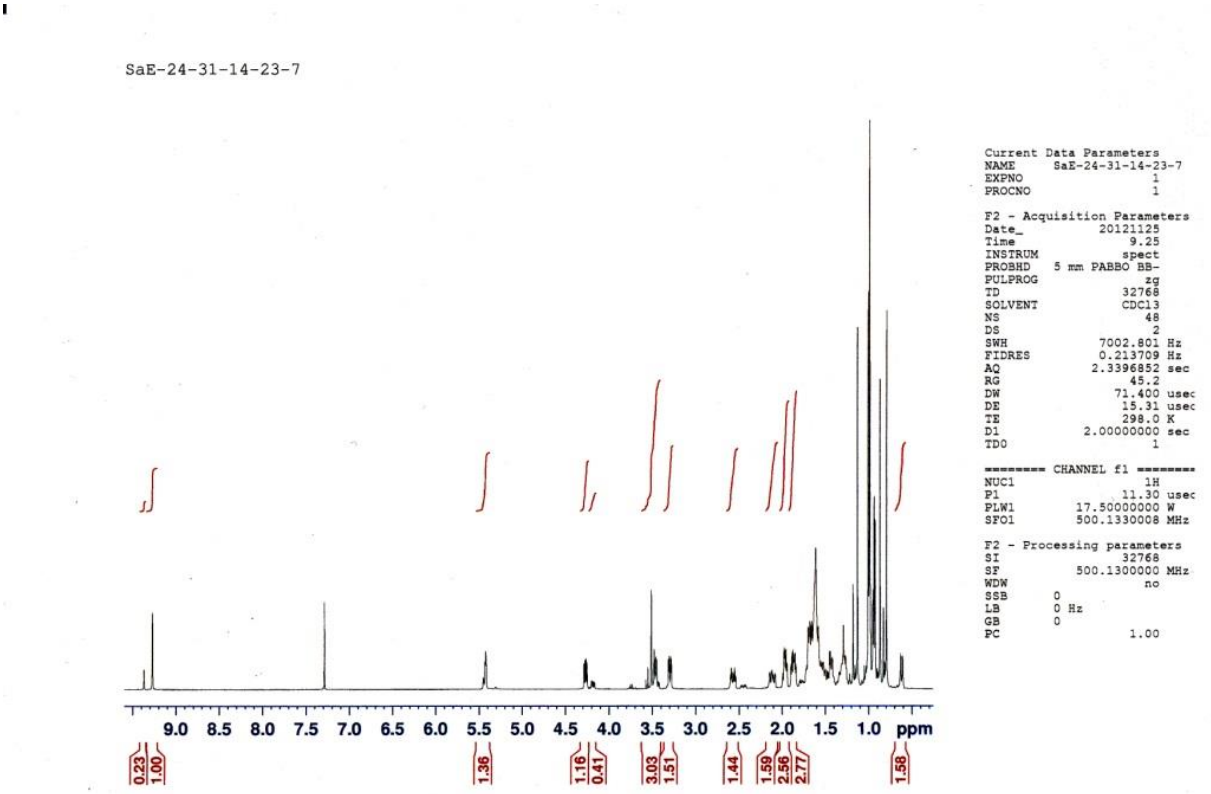


S29: NOESY (500 MHz) Spectrum of Compound **4**

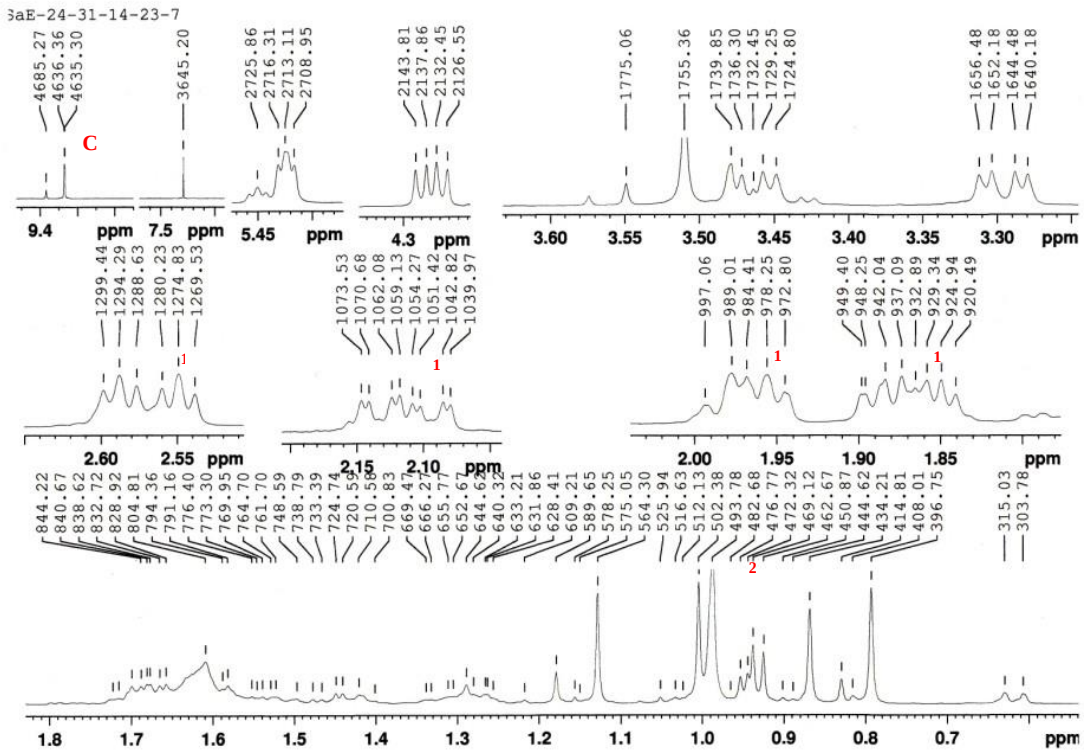


S30: HRESI-MS Spectrum of Compound **5**

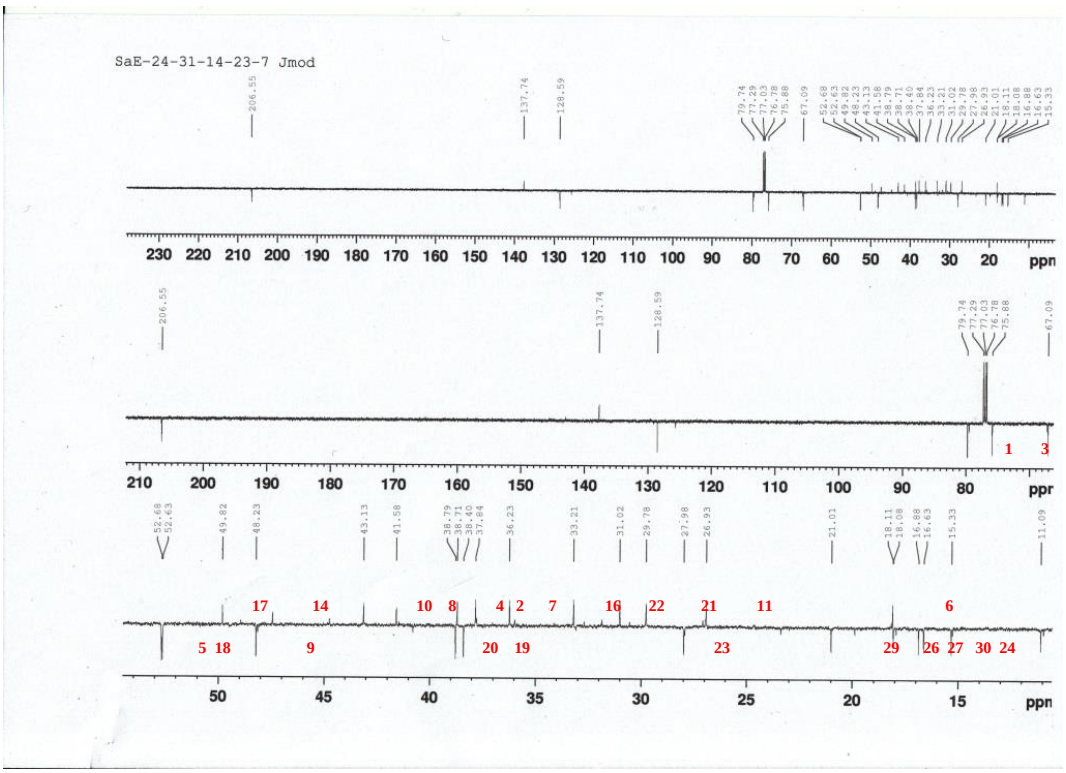
(1β, 3β, 15α-trihydroxyurs-12-en-28-al)



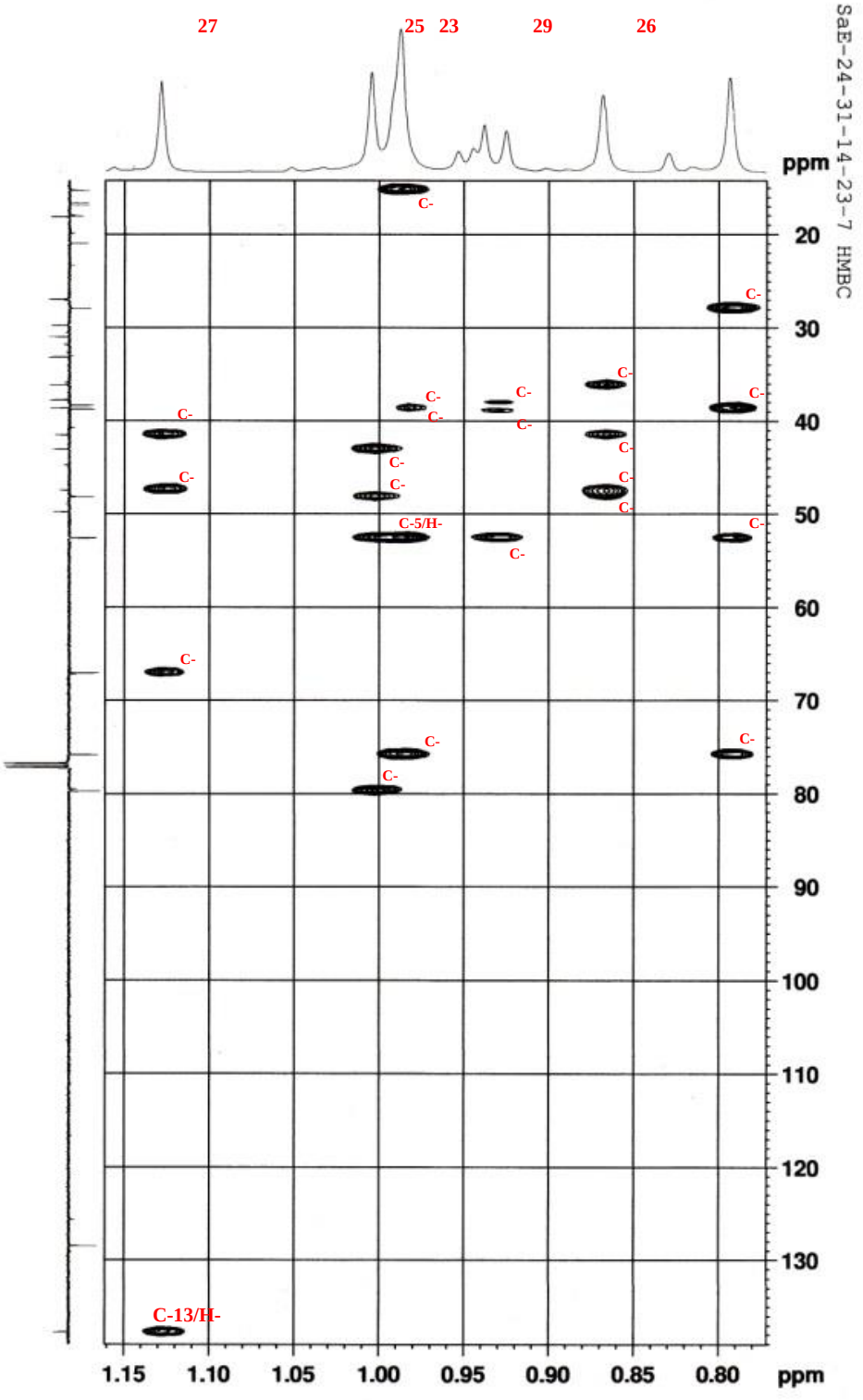
S31: ^{1}H-NMR (500 MHz, $CDCl_3$) Spectrum of Compound **5**



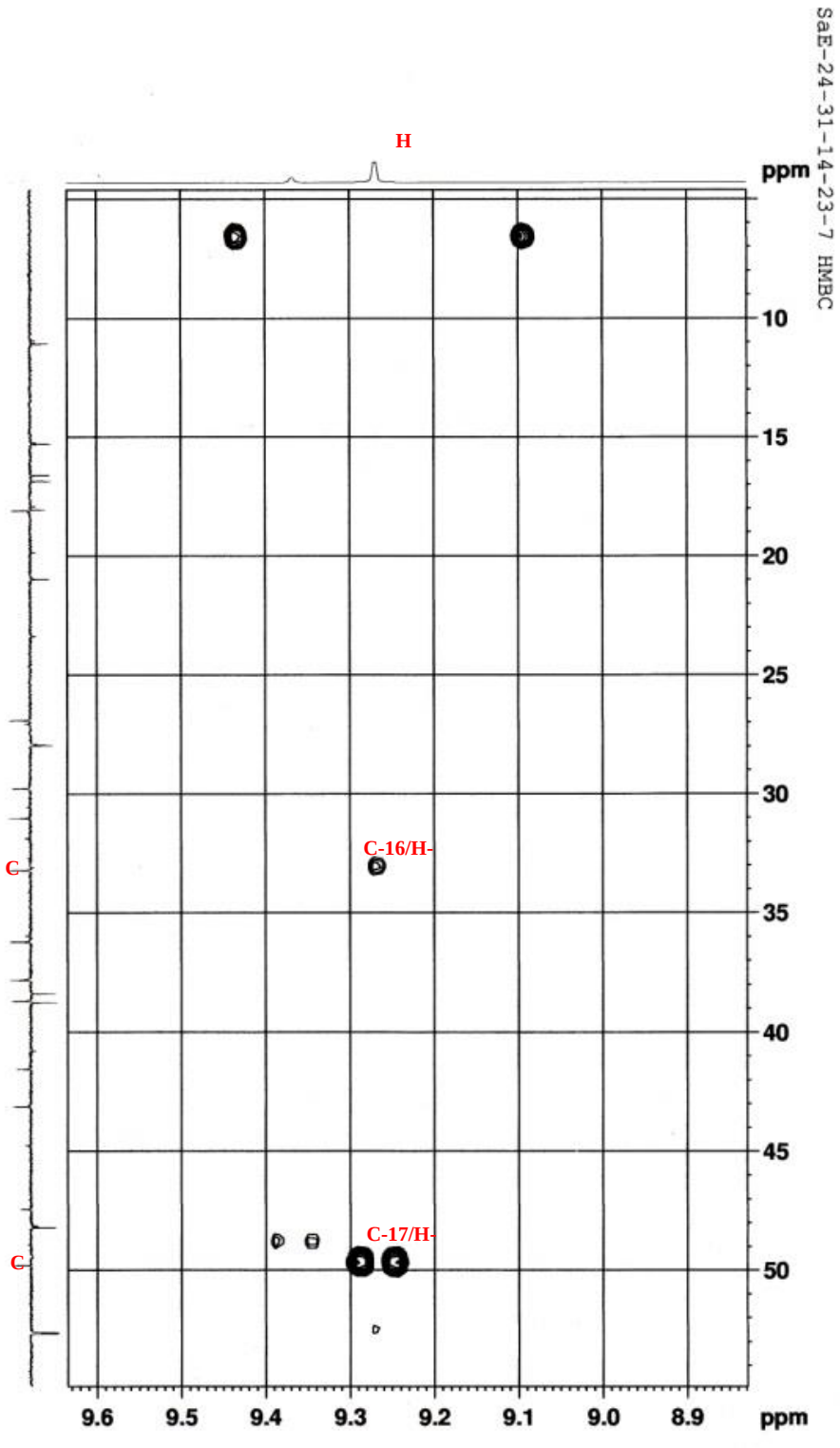
S32: ^{1}H-NMR (500 MHz, $CDCl_3$) Spectrum of Compound **5**



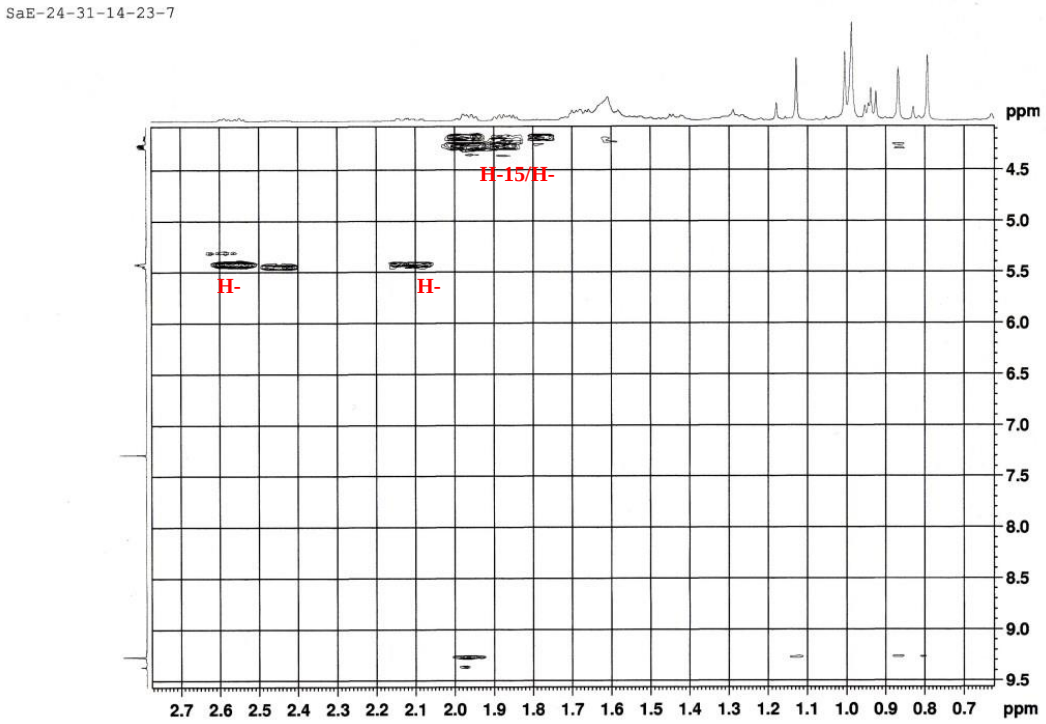
S33: ^{13}C-NMR J- mode (125 MHz, $CDCl_3$) Spectrum of Compound **5**



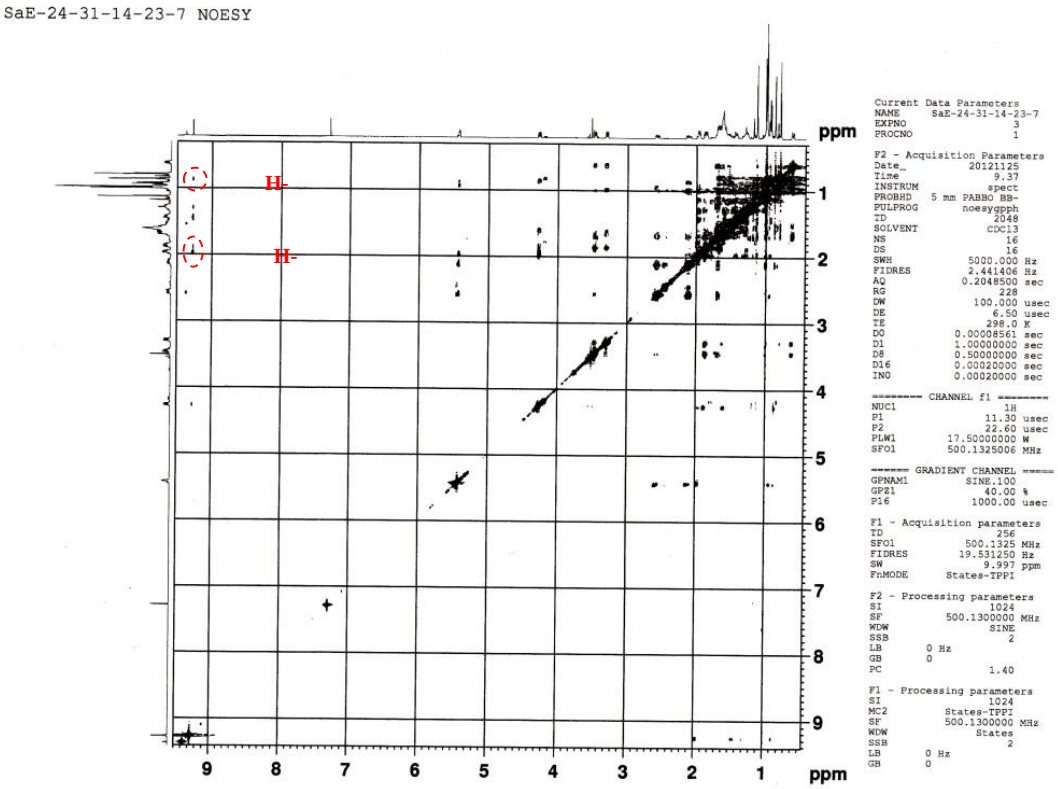
S34: HMBC (500 MHz) Spectrum of Compound **5** (From 14 to 140 ppm)



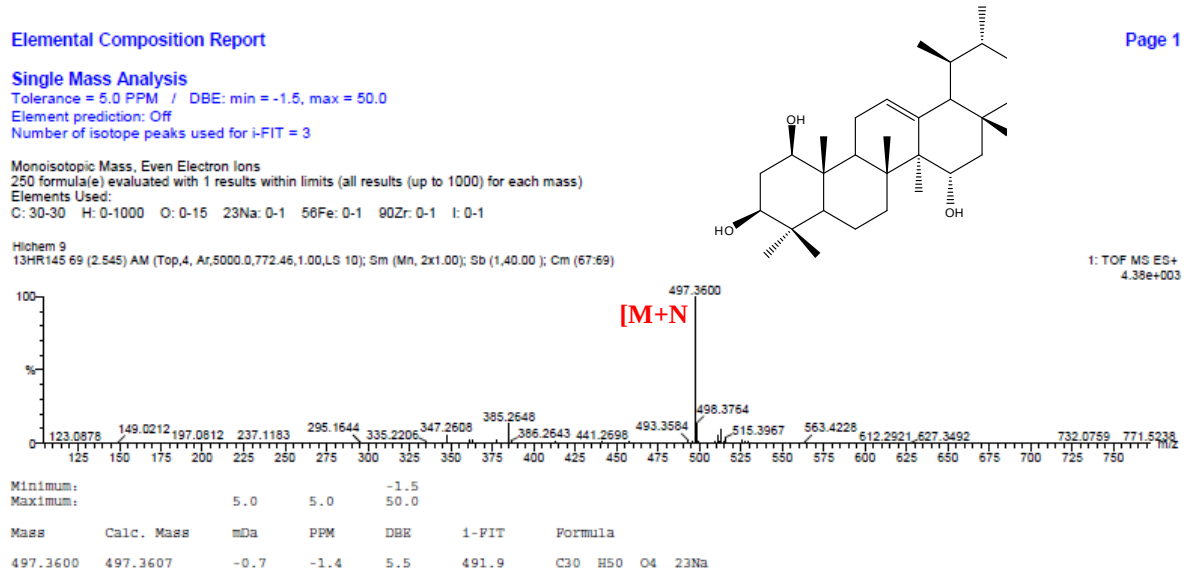
S35: HMBC (500 MHz) Spectrum of Compound **5** (From 5 to 55 ppm)



S36: COSY (500 MHz) Spectrum of Compound **5** (From 4.1 to 9.5 ppm)

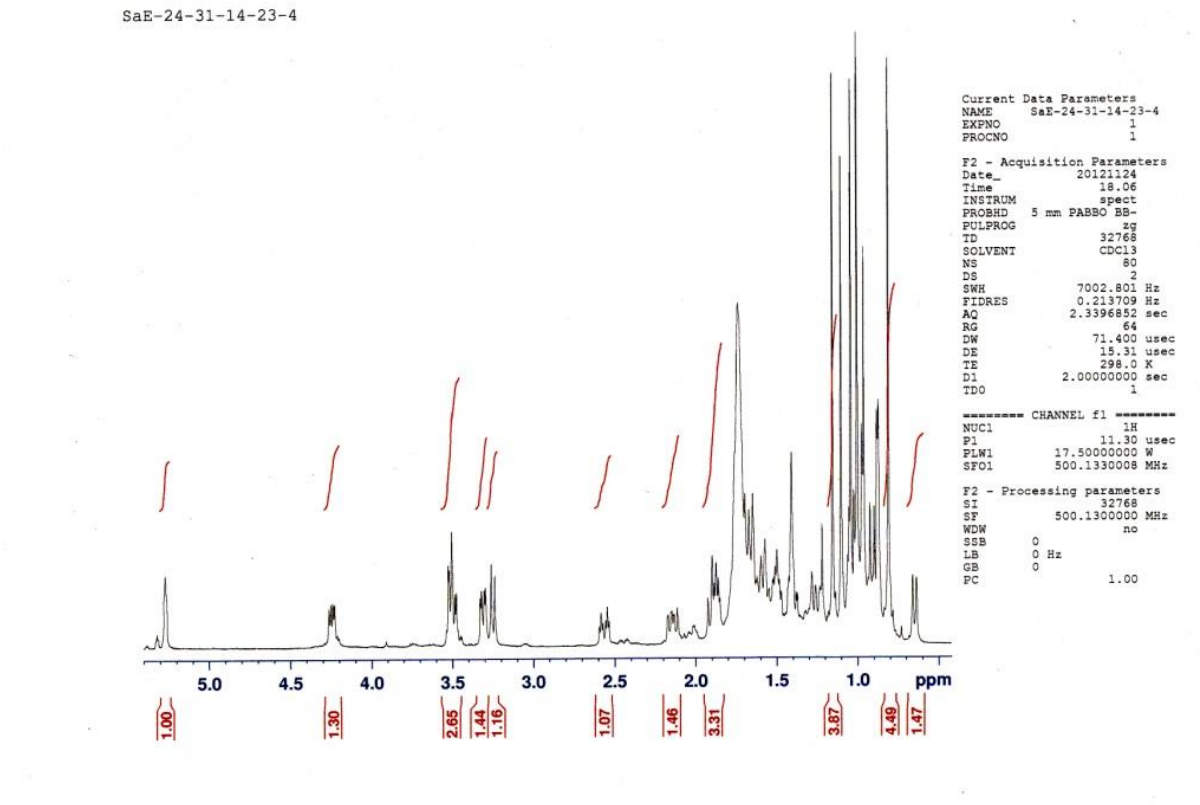


S37: NOESY (500 MHz) Spectrum of Compound **5**

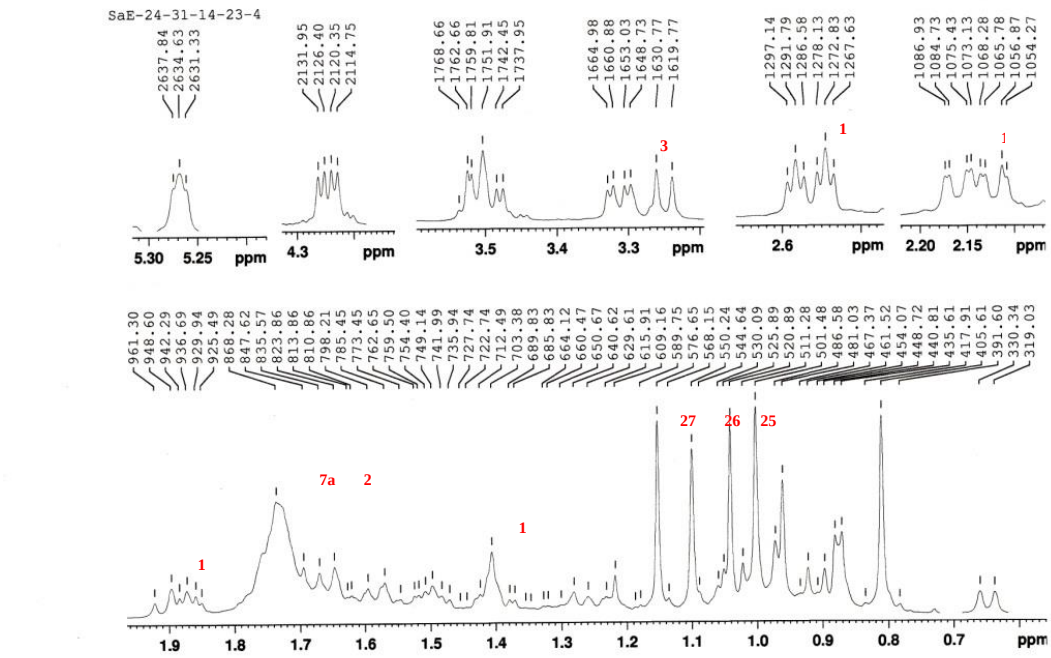


S38: HRESI-MS Spectrum of Compound **6**

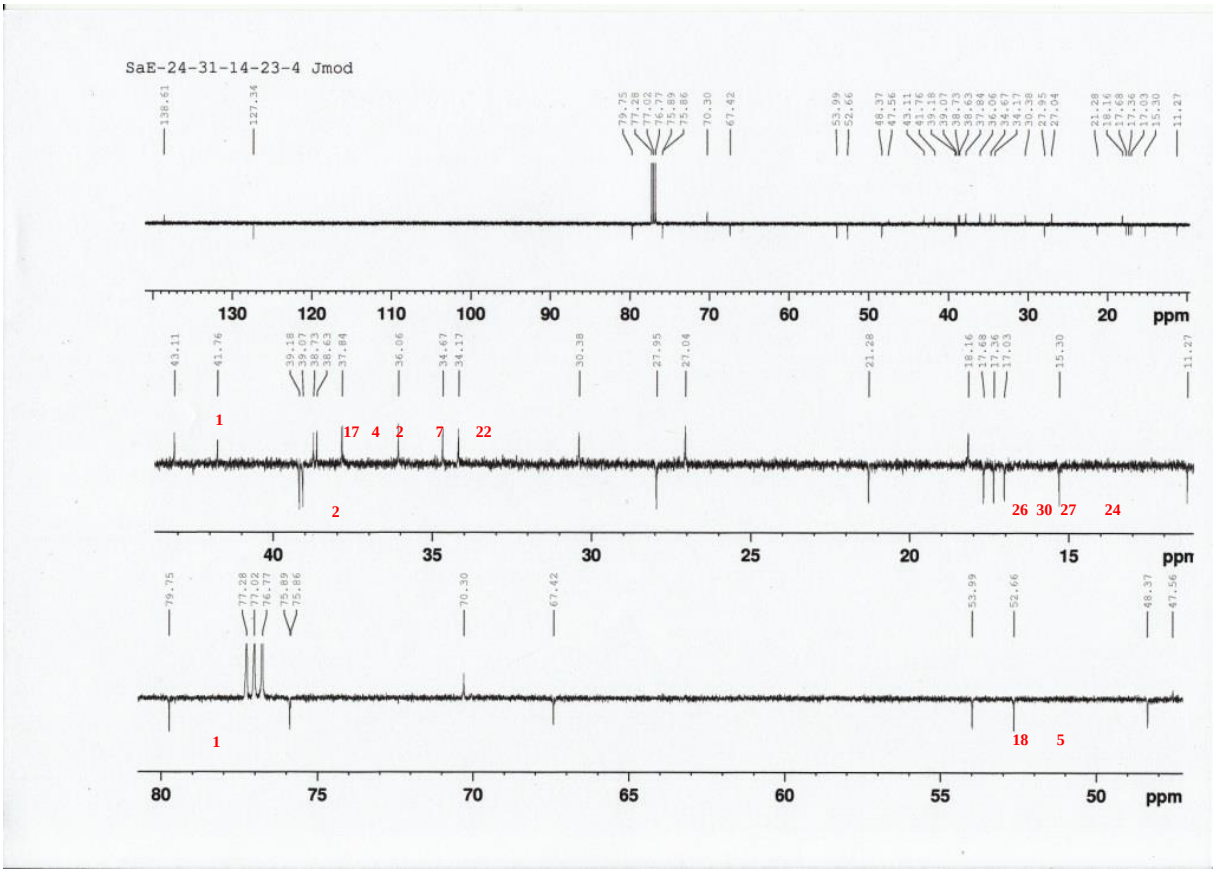
(Urs-12-ene-1β, 3β, 15α, 28β-tetraol)



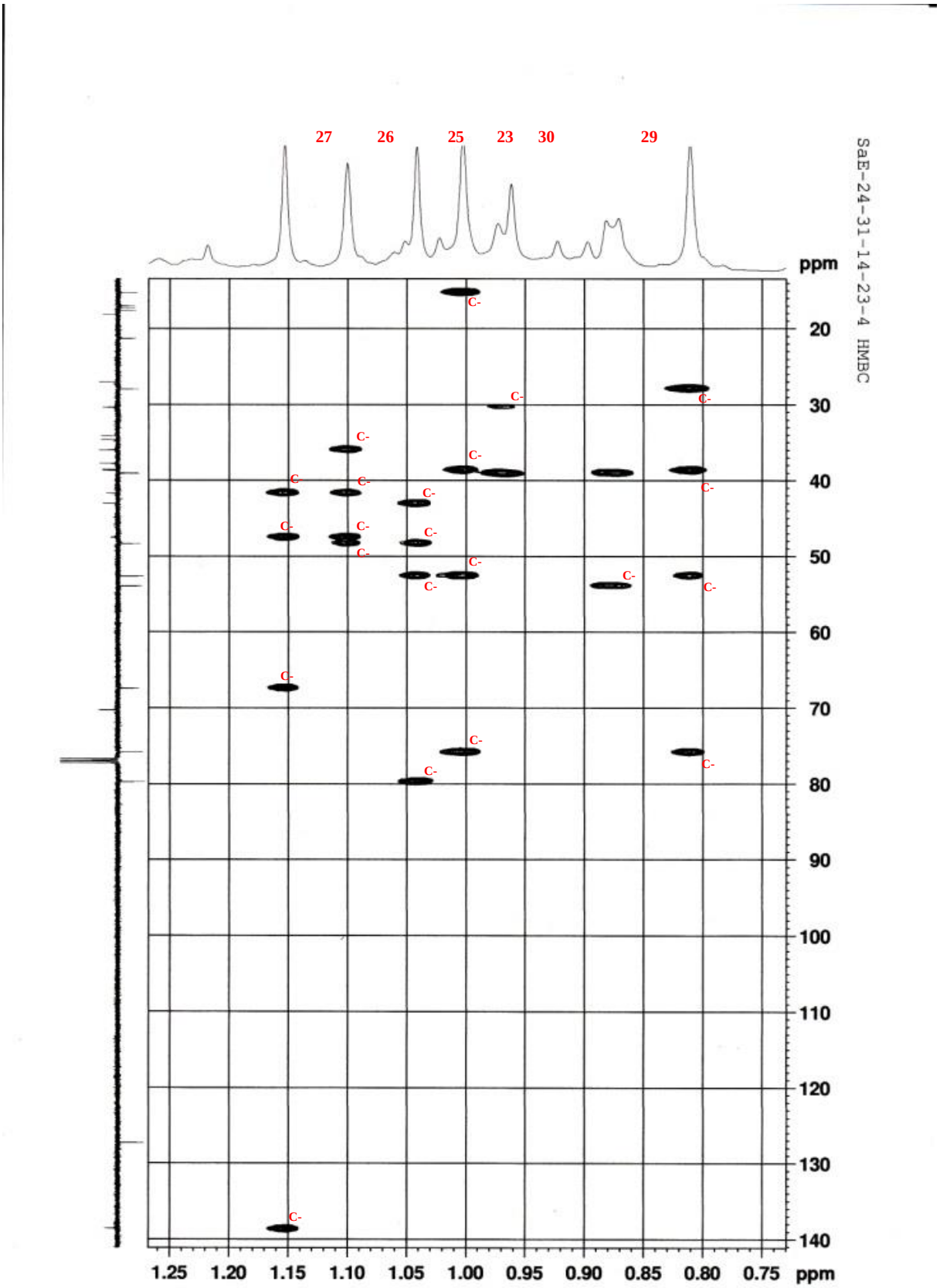
S39: ^{1}H-NMR (500 MHz, $CDCl_3$) Spectrum of Compound **6**



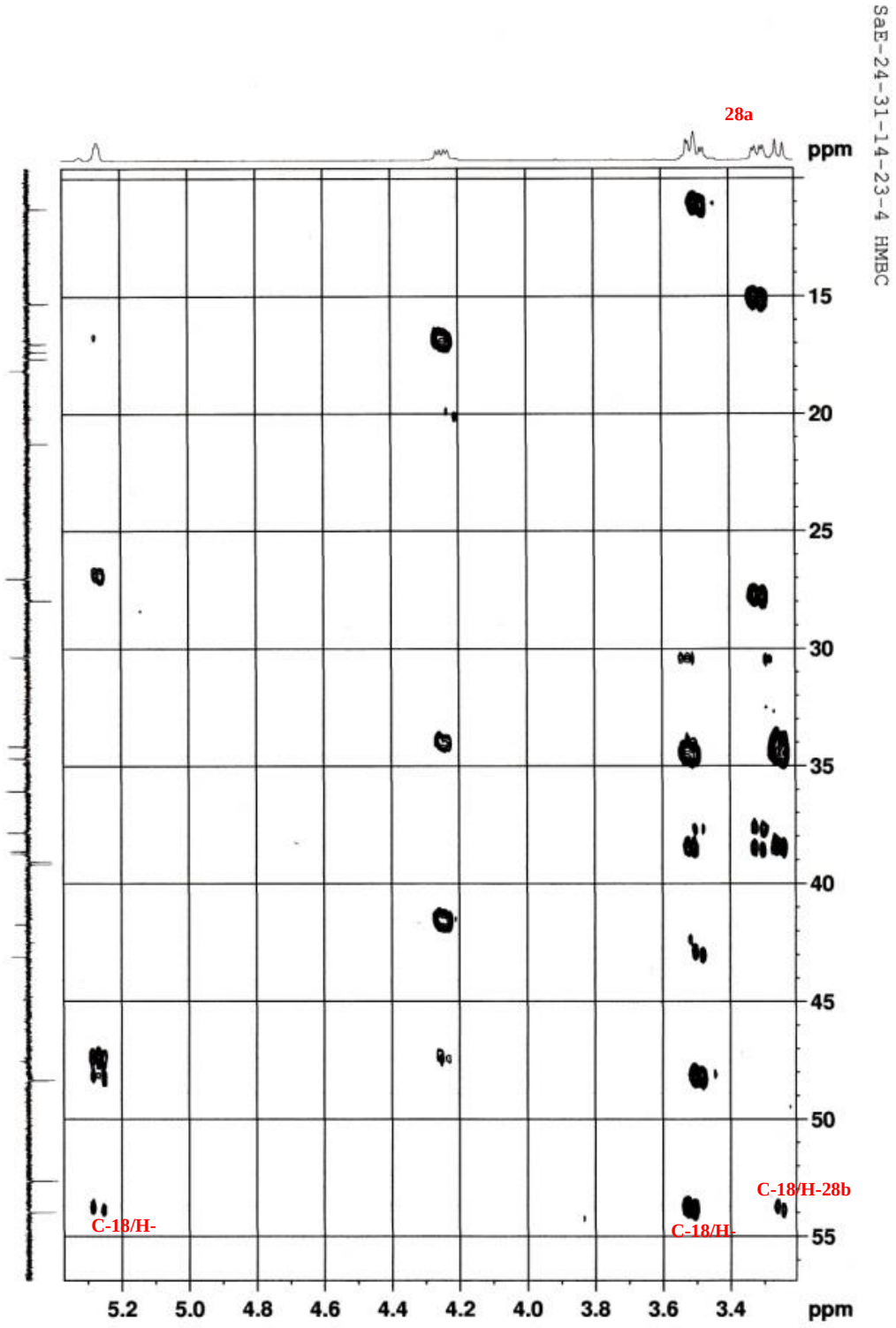
S40: ^{1}H-NMR (500 MHz, $CDCl_3$) Spectrum of Compound **6**



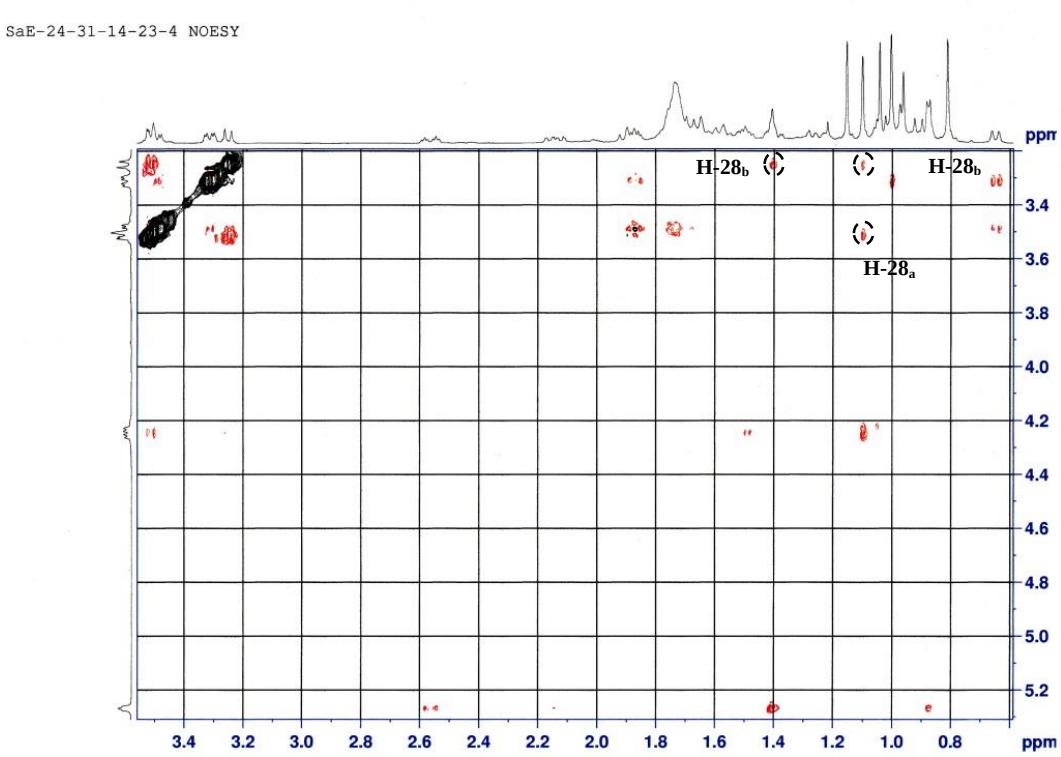
S41: ^{13}C-NMR J- mode (125 MHz, $CDCl_3$) Spectrum of Compound **6**



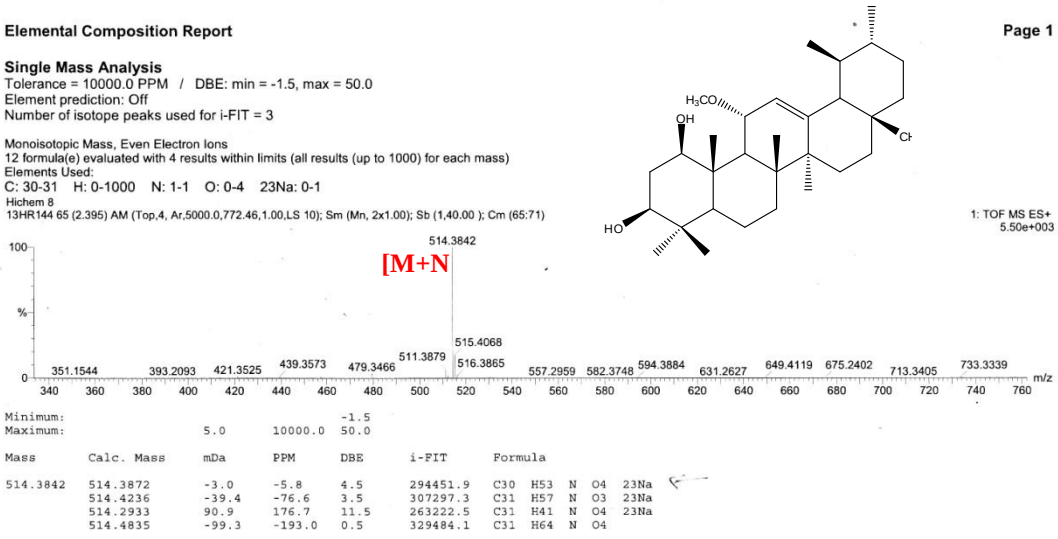
S42: HMBC (500 MHz) Spectrum of Compound **6** (From 13 to 141 ppm)



S43: HMBC (500 MHz) Spectrum of Compound **6** (From 10 to 57 ppm)

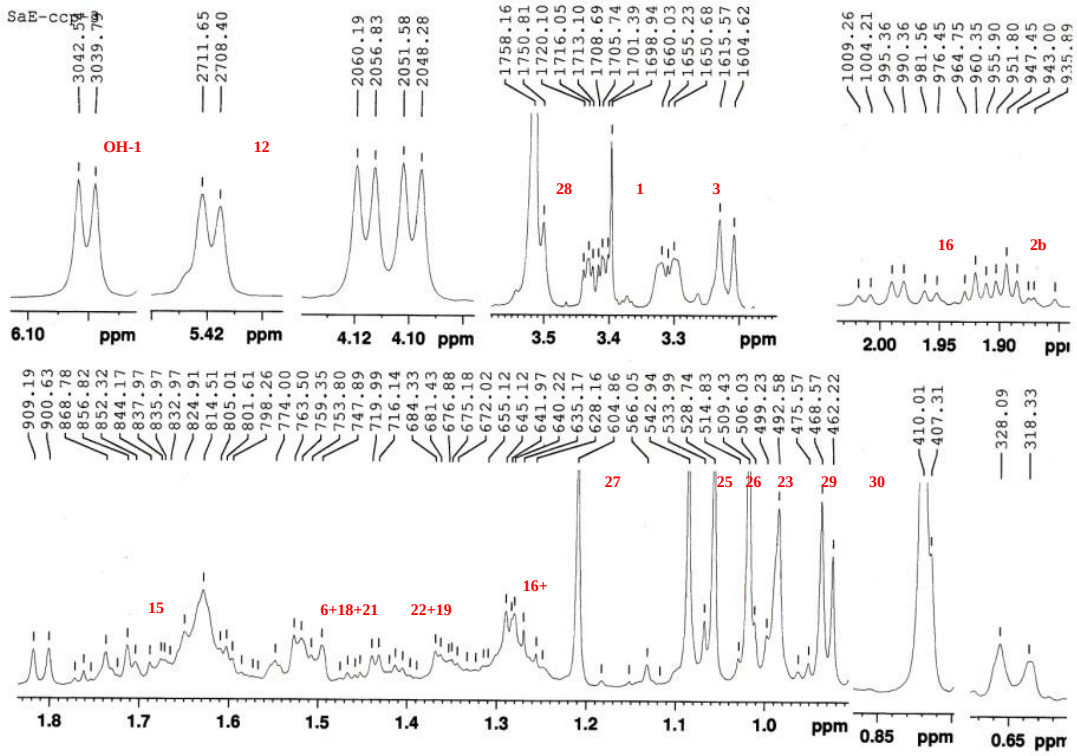


S44: NOESY (500 MHz) Spectrum of Compound **6** (From 3.2 to 5.3 ppm)

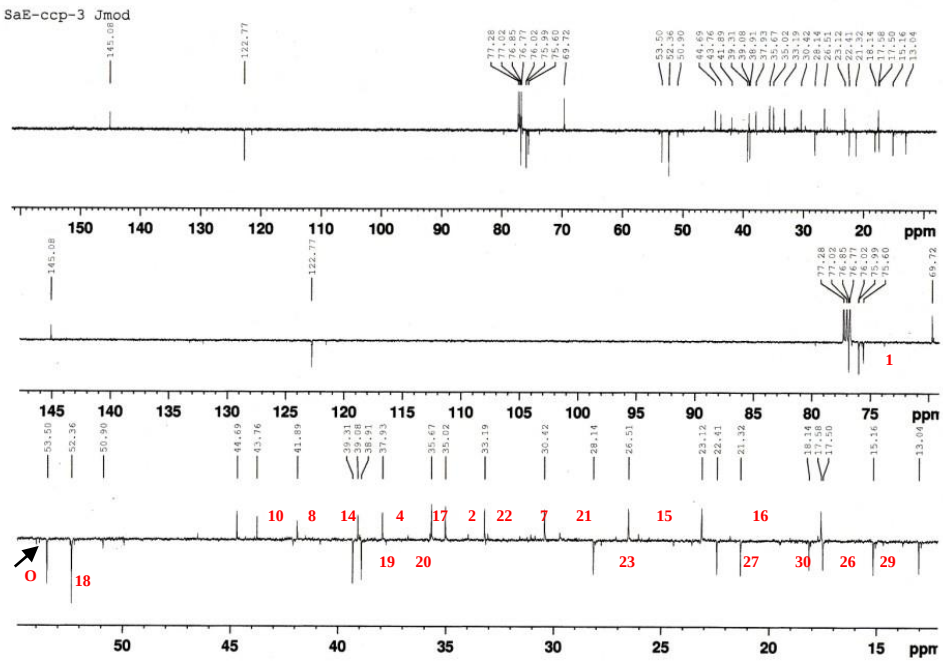


S45: HRESI-MS Spectrum of Compound **7**

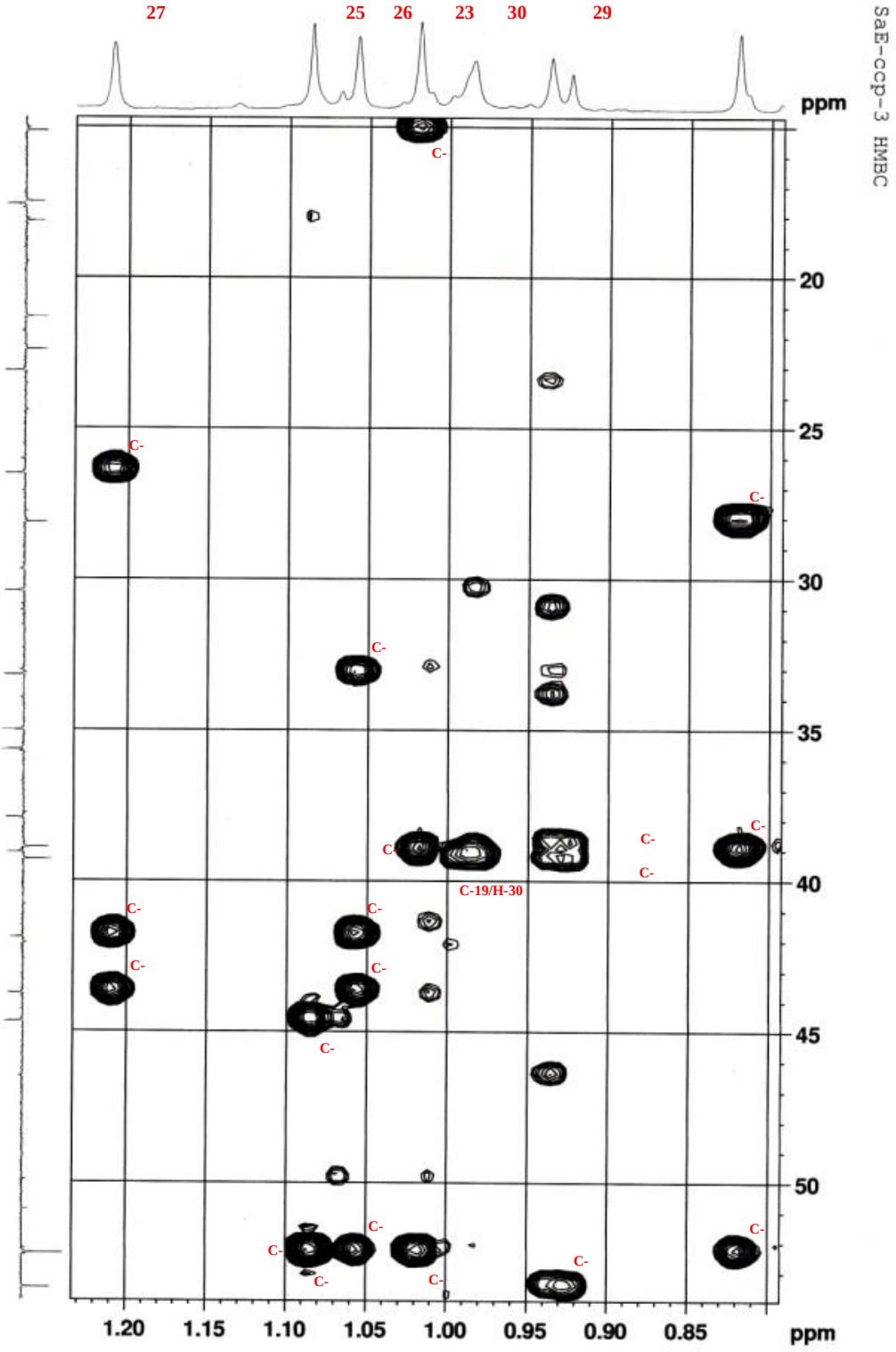
(11α-Methoxyurs-12-ene-1β, 3β, 28β-triol)



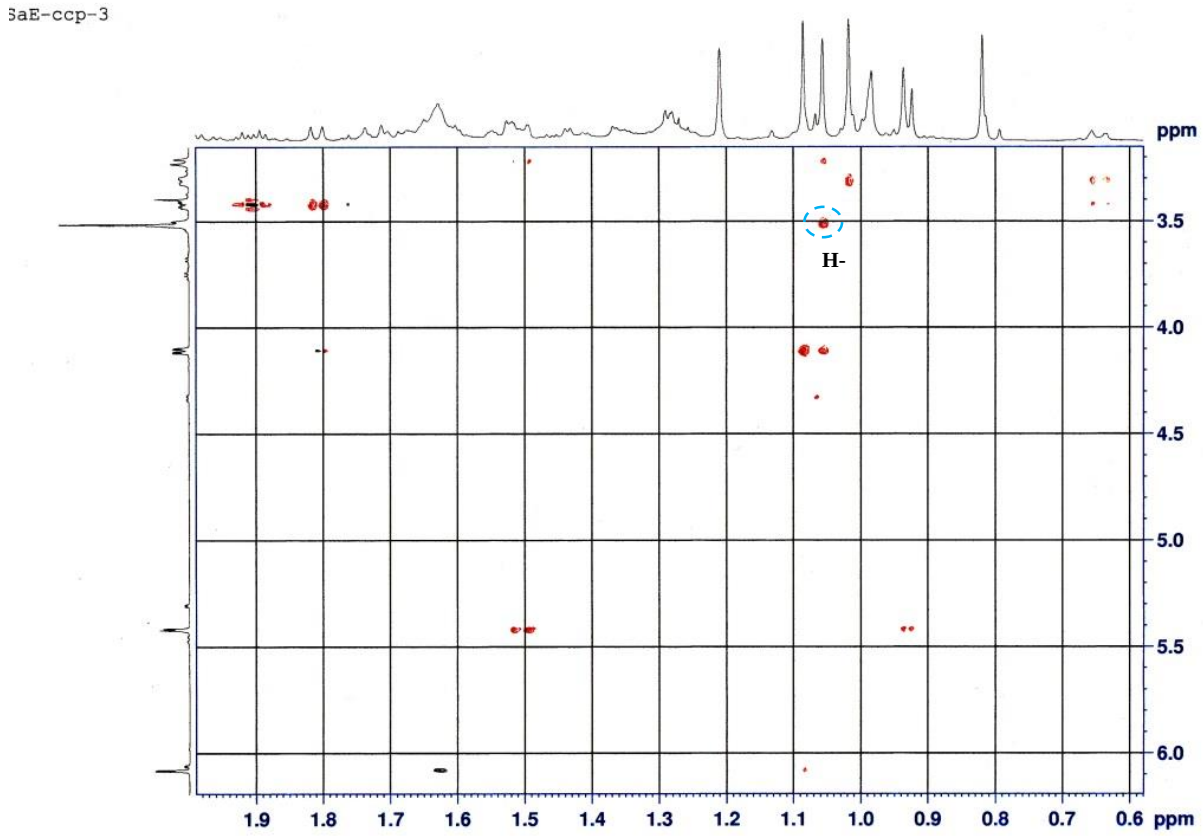
S46: ^{1}H-NMR (500 MHz, $CDCl_3$) Spectrum of Compound **7**



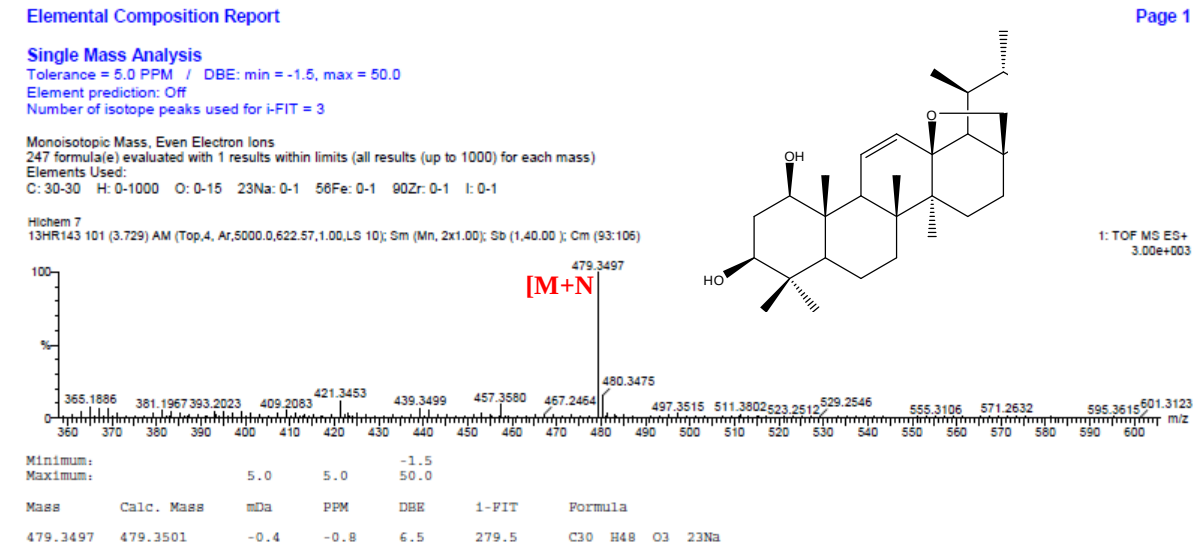
S47: ^{13}C-NMR J- mode (125 MHz, $CDCl_3$) Spectrum of Compound **7**



S48: HMBC (500 MHz) Spectrum of Compound **7** (From 15 to 55 ppm)

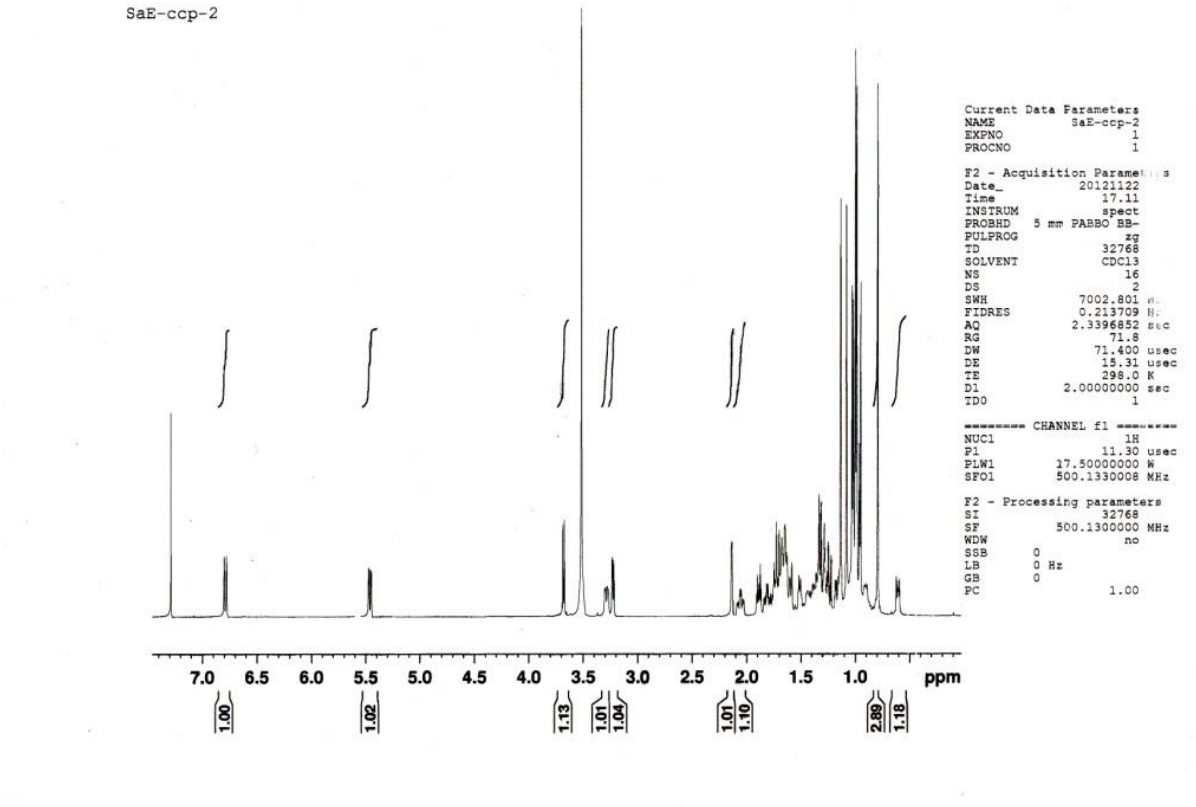


S49: NOESY (500 MHz) Spectrum of Compound **7** (From 3.2 to 6.2 ppm)

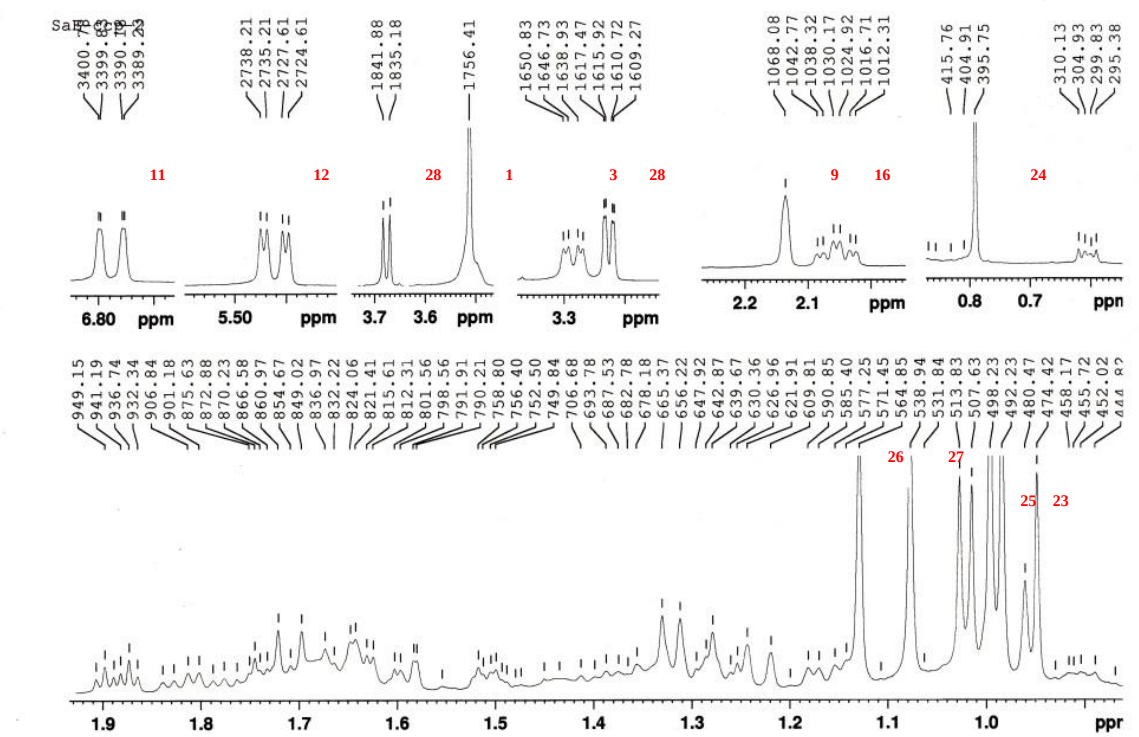


S50: HRESI-MS Spectrum of Compound **8**

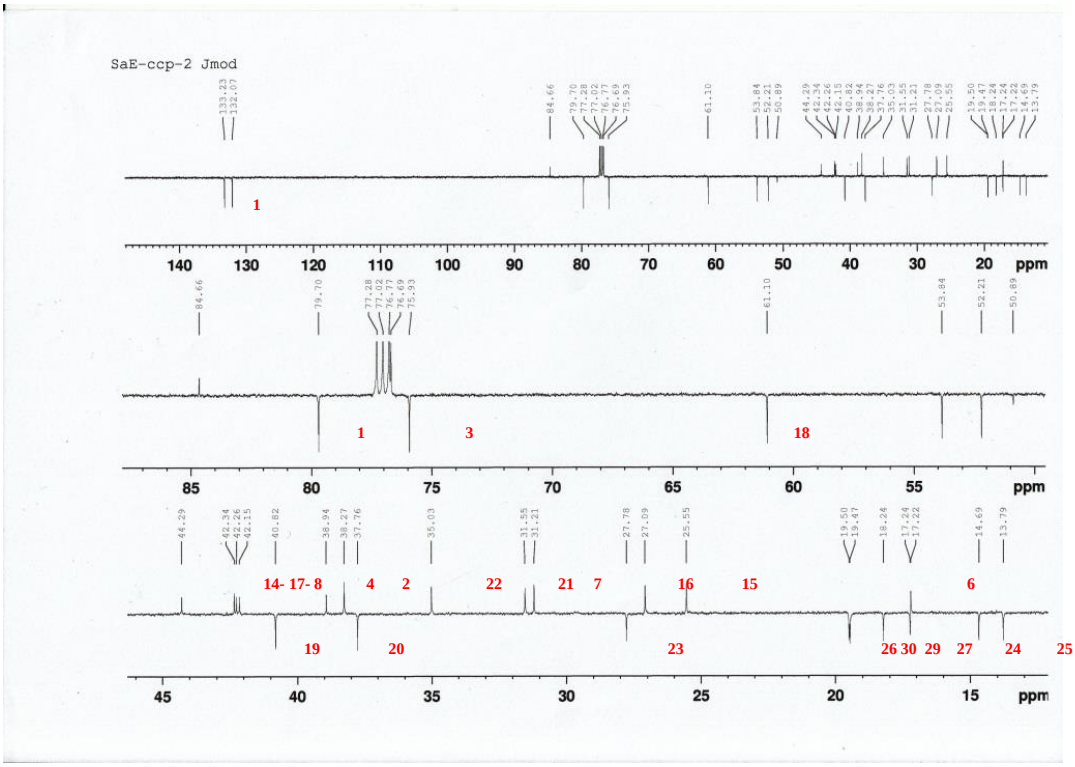
(13β, 28β-Epoxy-urs-12-ene-1β, 3β-diol)



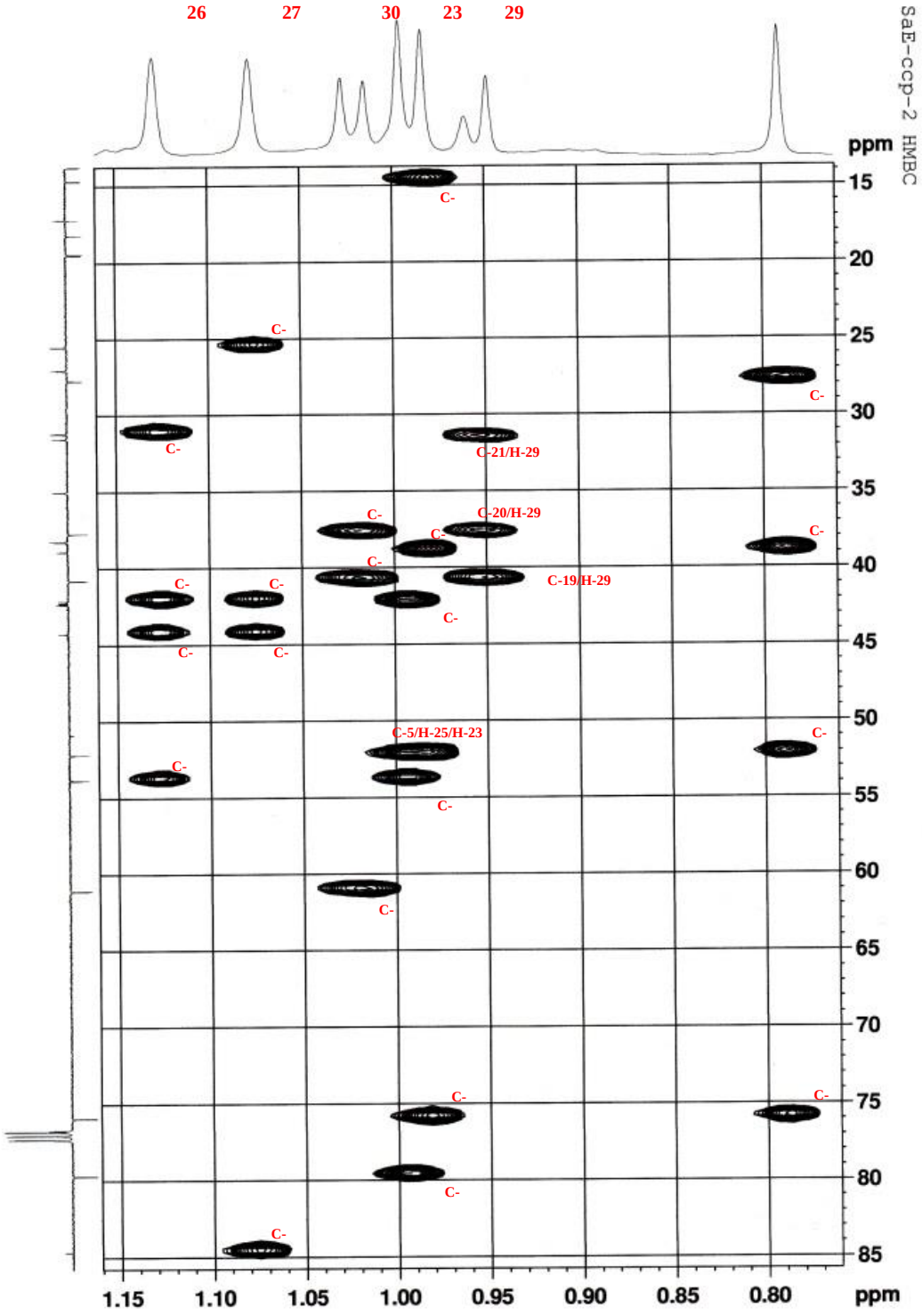
S51: ^{1}H-NMR (500 MHz, $CDCl_3$) Spectrum of Compound **8**



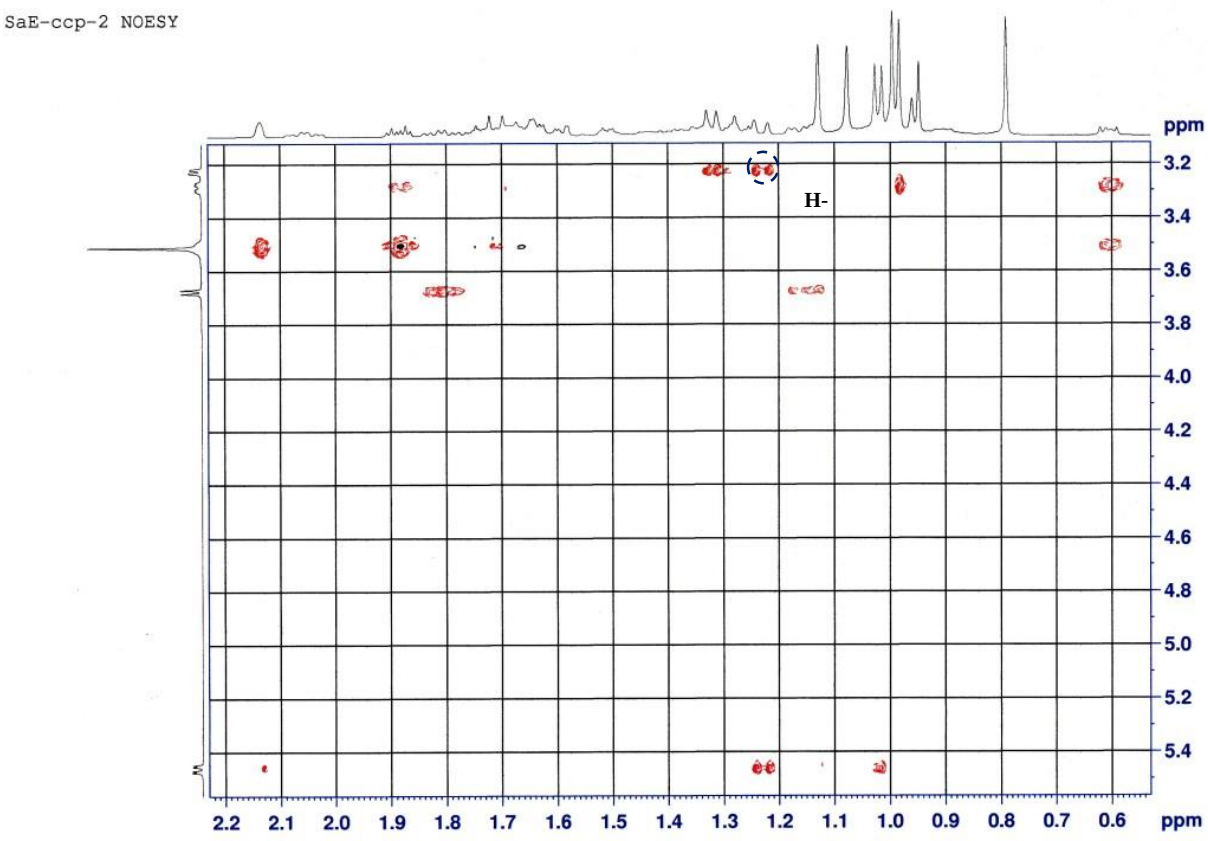
S52: ^{1}H-NMR (500 MHz, $CDCl_3$) Spectrum of Compound **8**



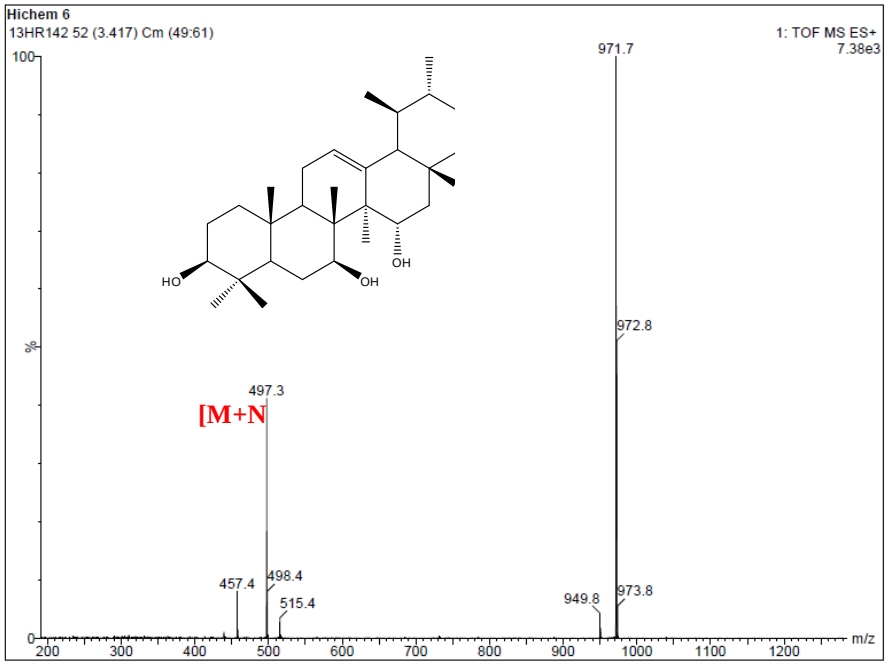
S53: ^{13}C-NMR J- mode (125 MHz, $CDCl_3$) Spectrum of Compound **8**



S54: HMBC (500 MHz) Spectrum of Compound **8** (From 14 to 86 ppm)

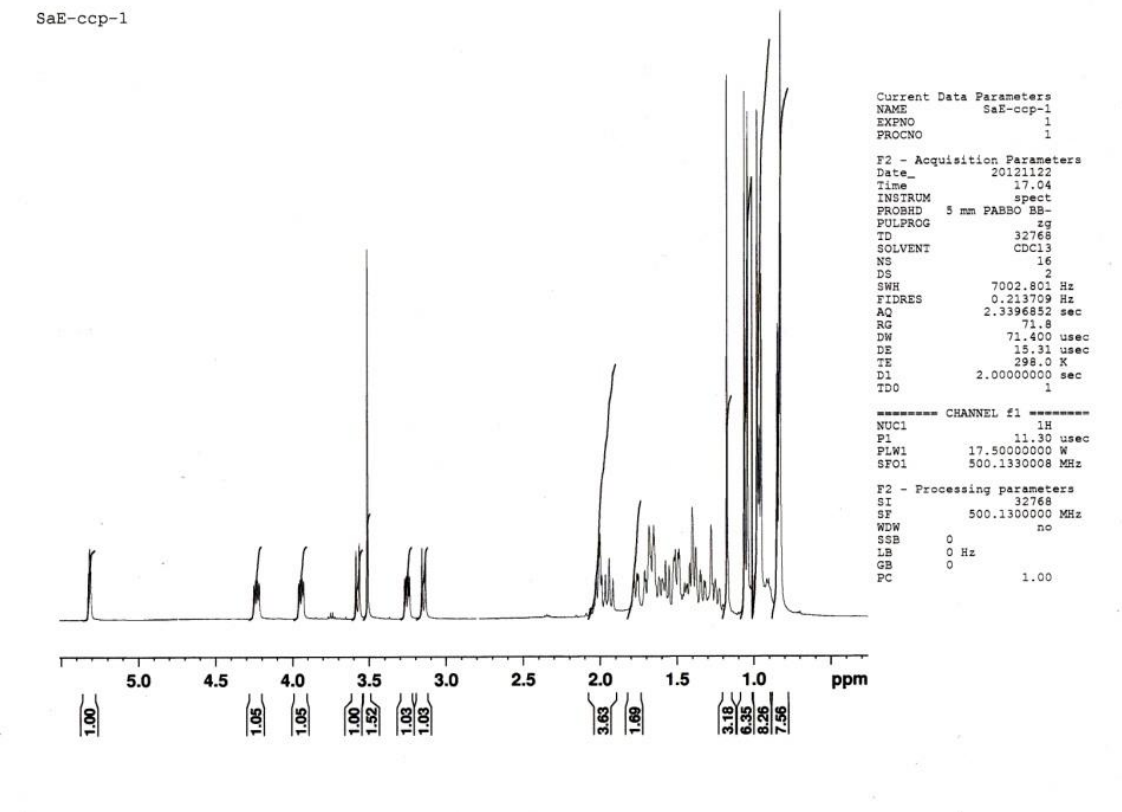


S55: NOESY (500 MHz) Spectrum of Compound **8** (From 3.1 to 5.6 ppm)

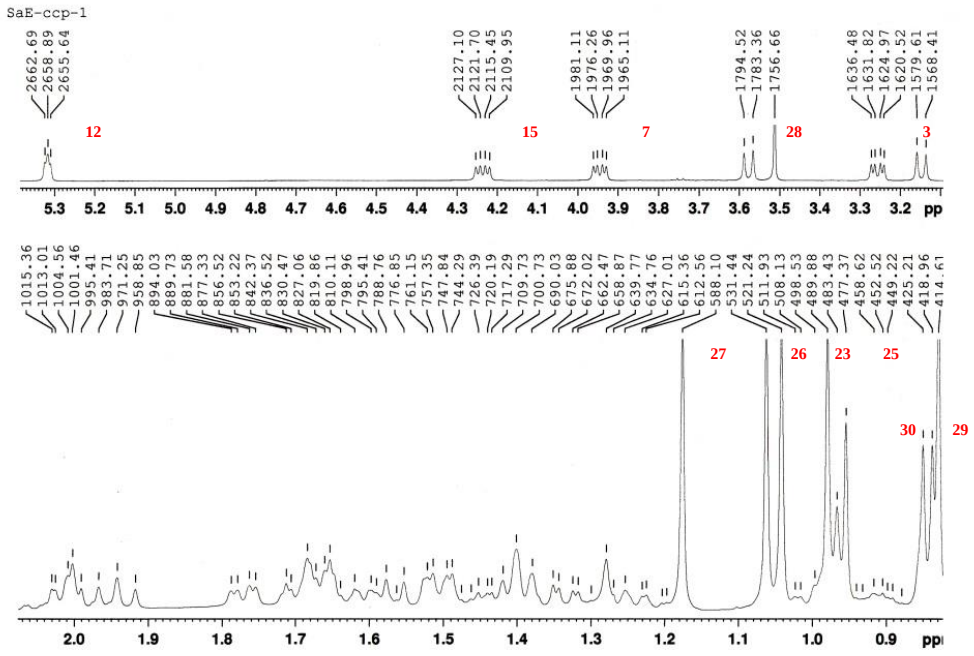


S56: HRESI-MS Spectrum of Compound **9**

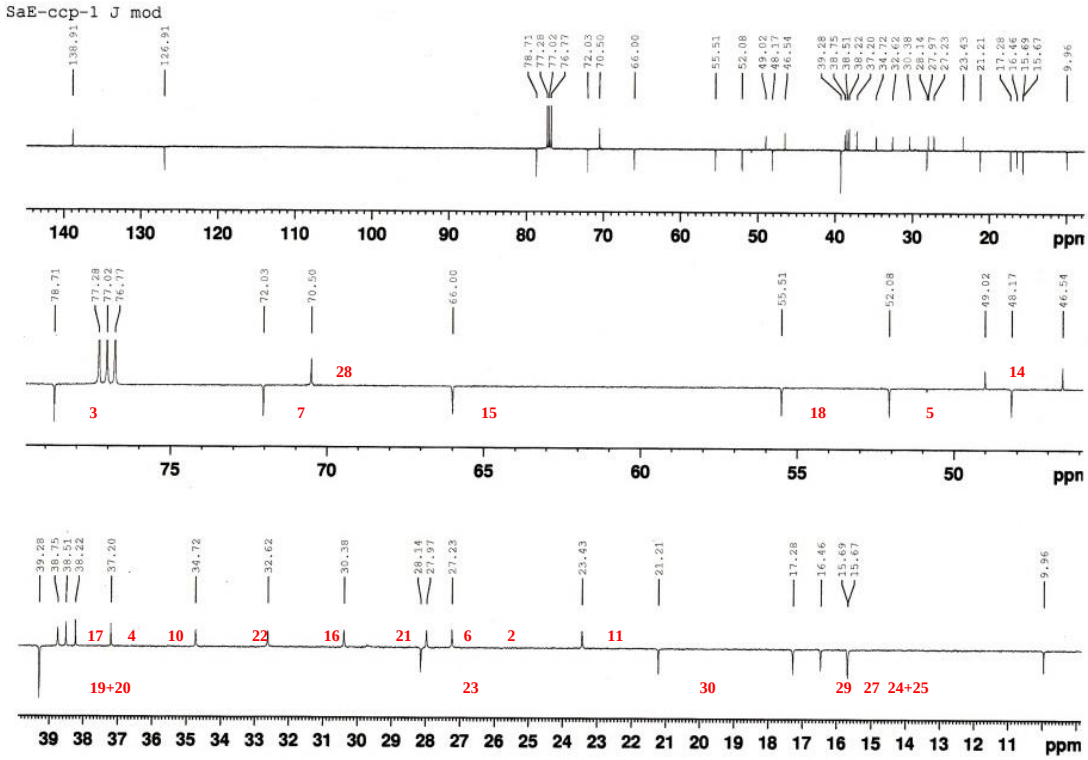
(Urs-12-ene-3β, 7β, 15α ,28β-tetraol)



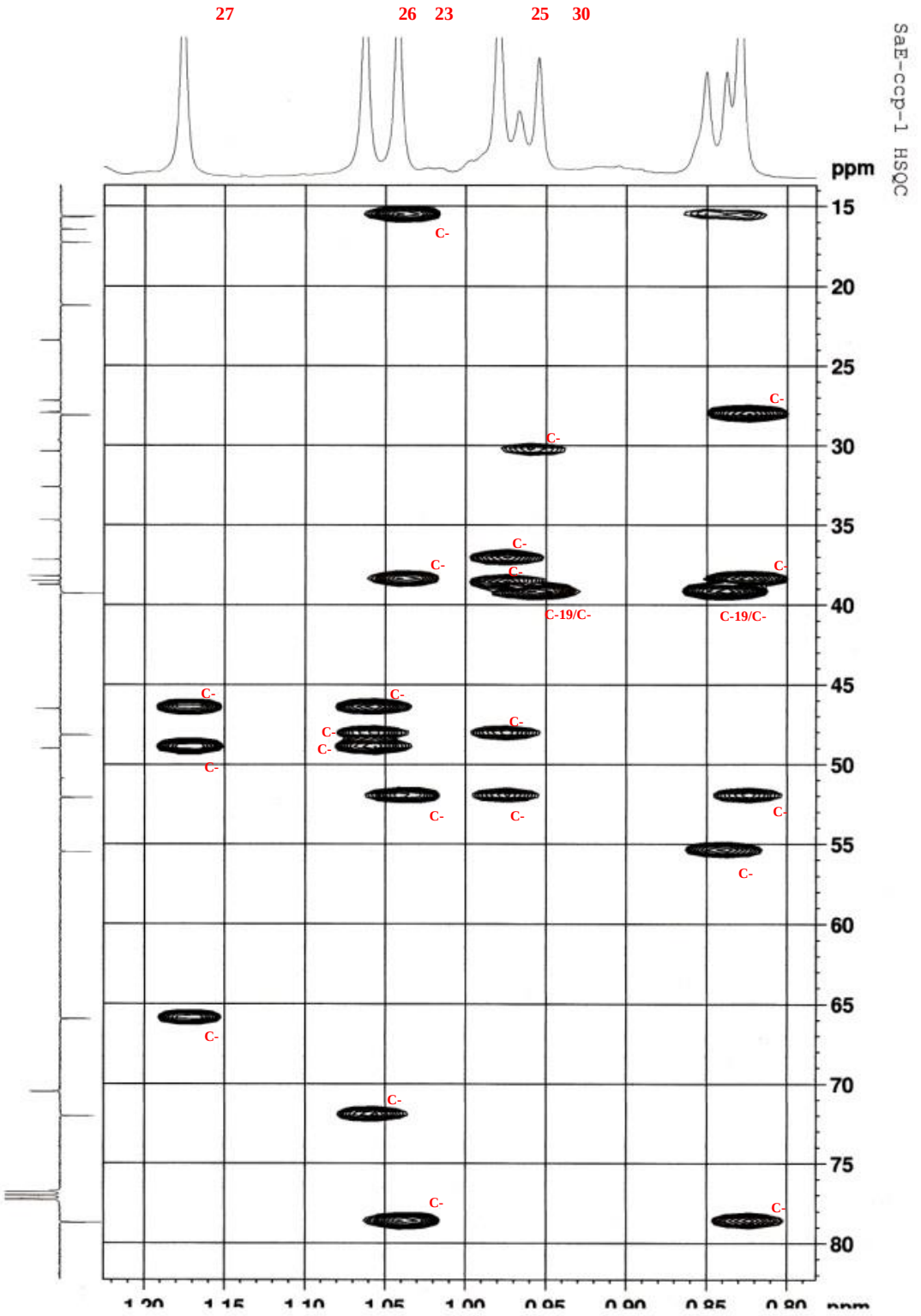
S57: ^{1}H-NMR (500 MHz, $CDCl_3$) Spectrum of Compound **9**



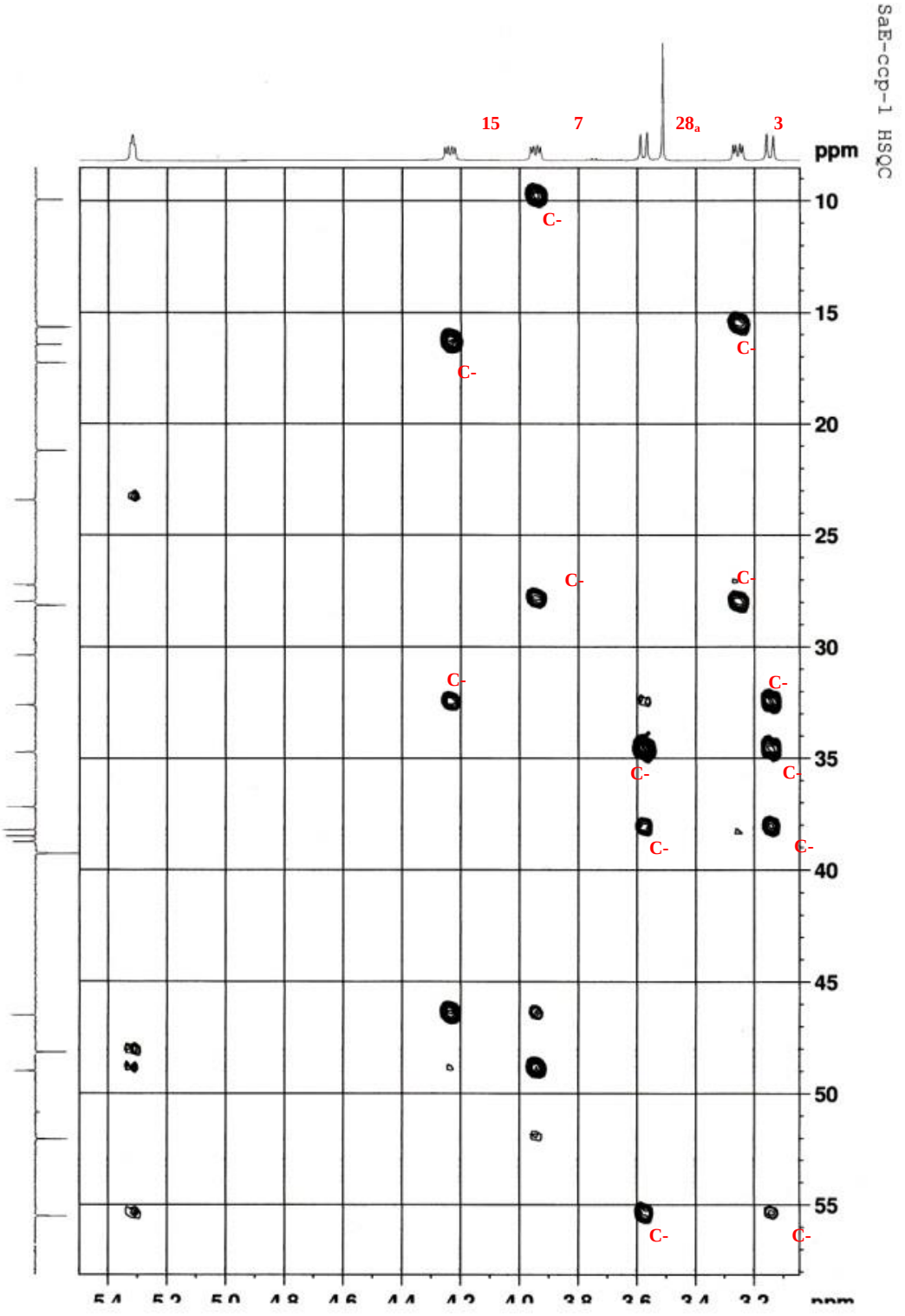
S58: ^{1}H-NMR (500 MHz, CDCl3) Spectrum of Compound **9**



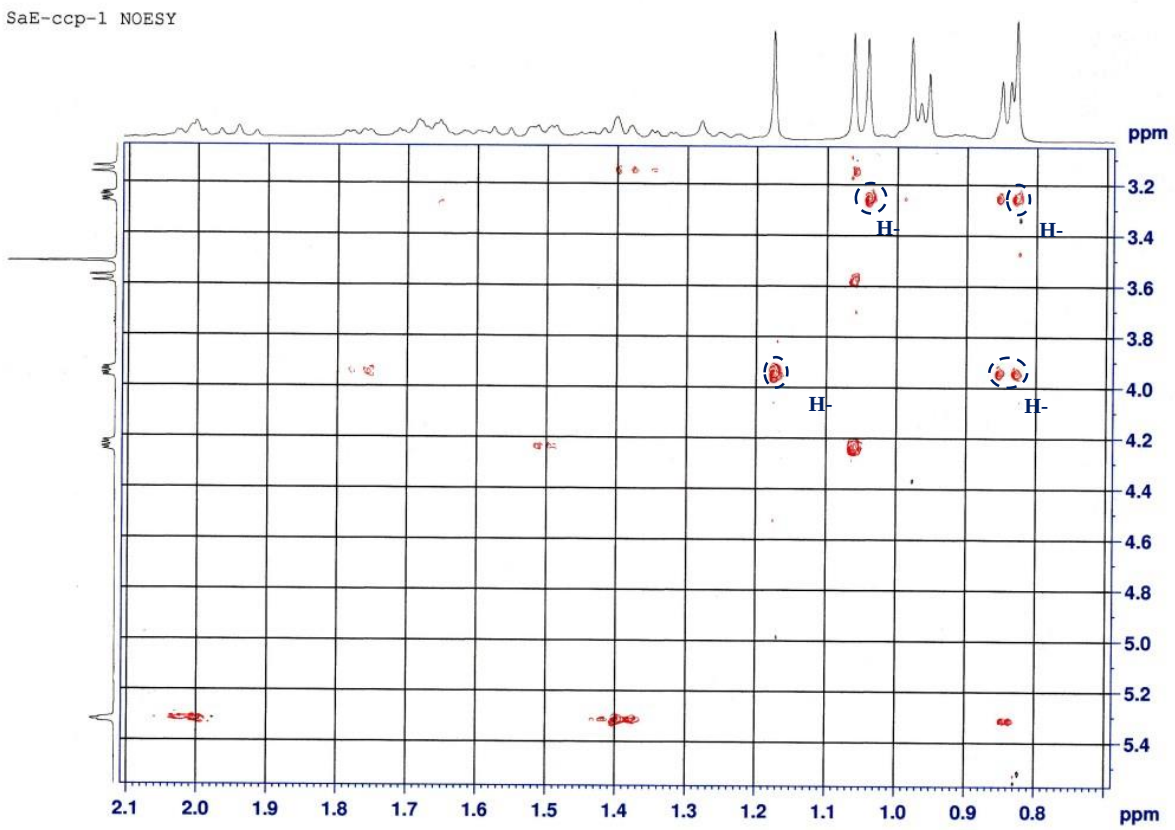
S59: ^{13}C-NMR J- mode (125 MHz, $CDCl_3$) Spectrum of Compound **9**



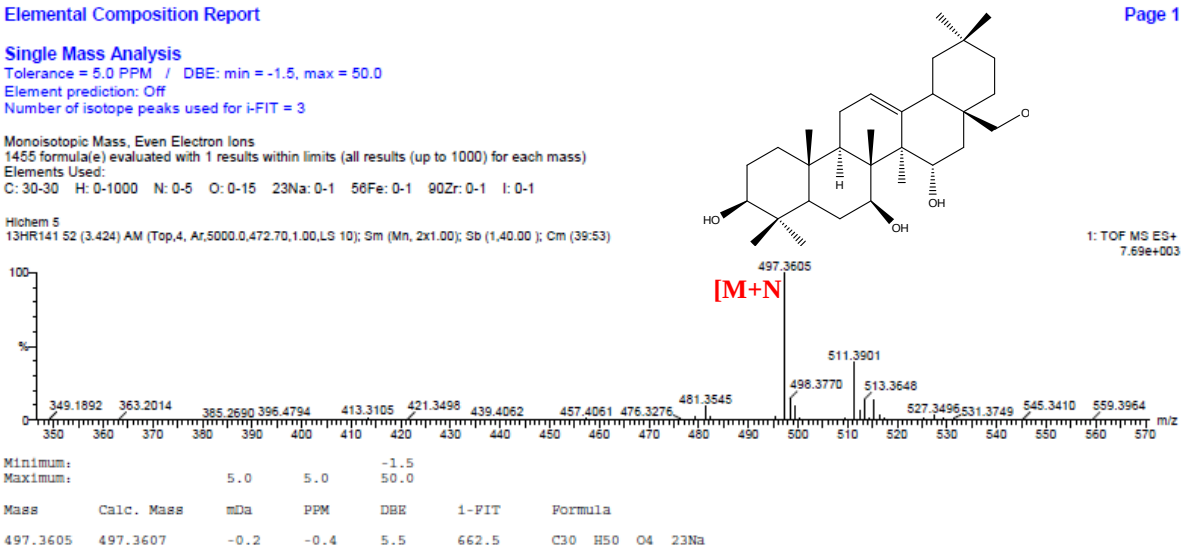
S60: HMBC (500 MHz) Spectrum of Compound **9** (From 14 to 82 ppm)



S61: HMBC (500 MHz) Spectrum of Compound **9** (From 11 to 58 ppm)

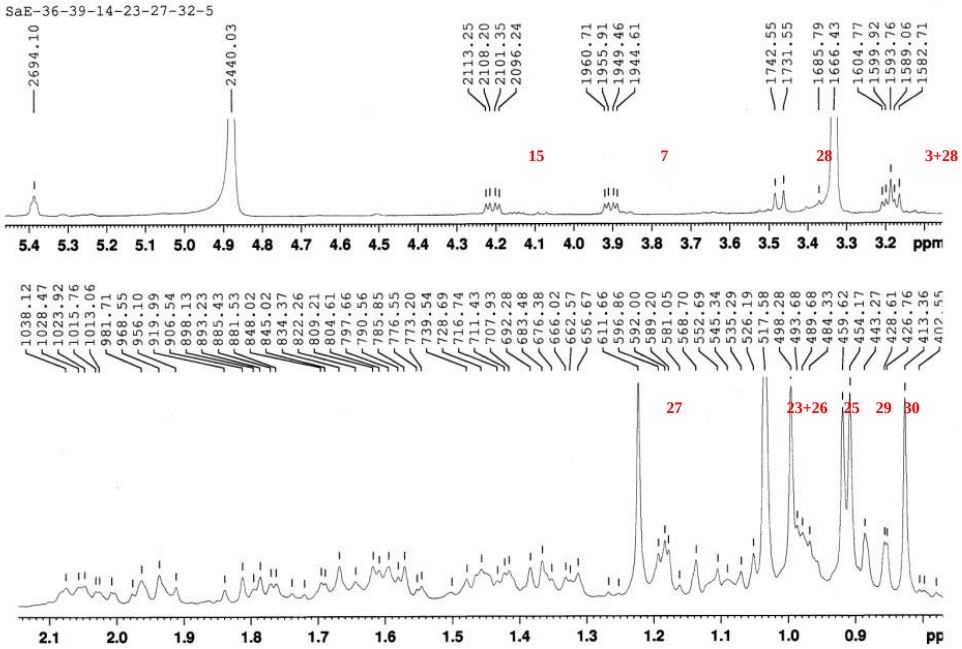


S62: NOESY (500 MHz) Spectrum of Compound **9** (From 3.1 to 5.6 ppm)

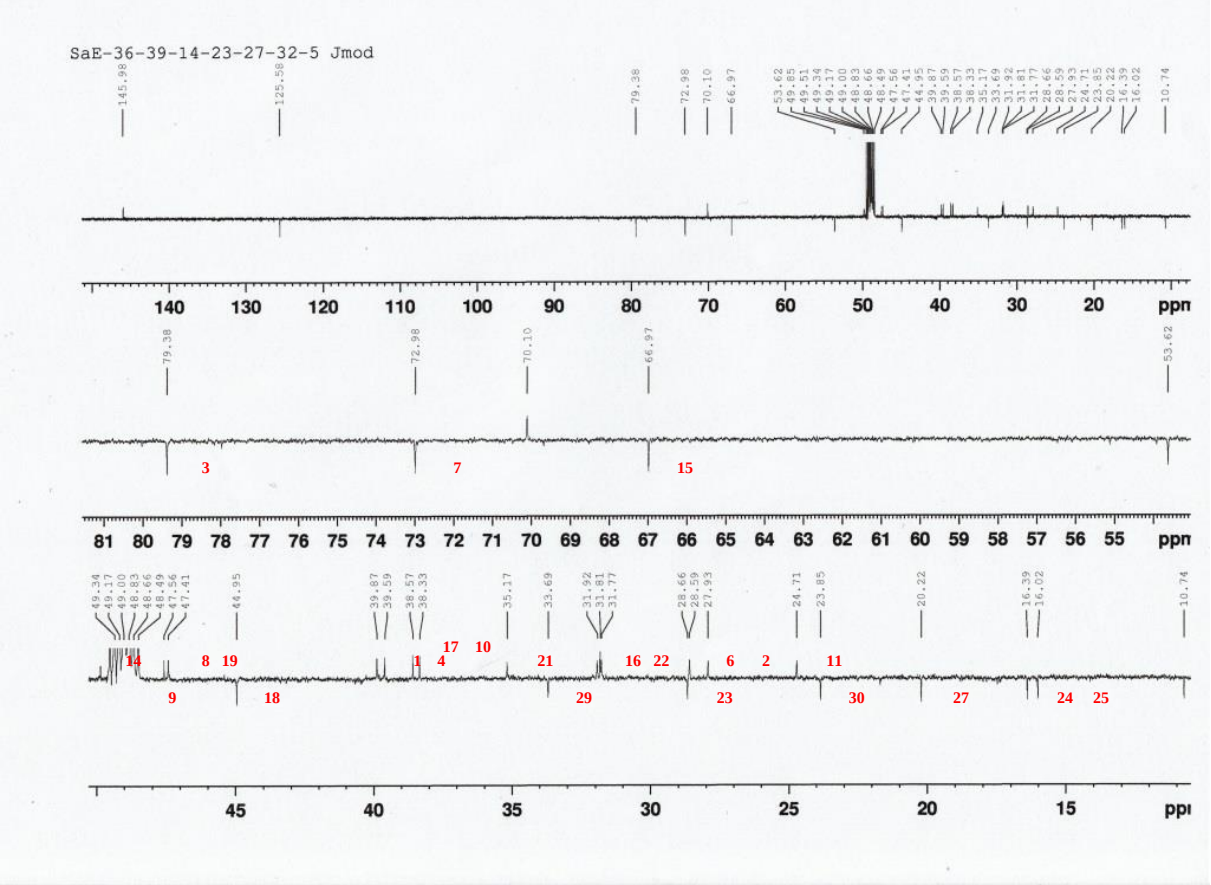


S63: HRESI-MS Spectrum of Compound **10**

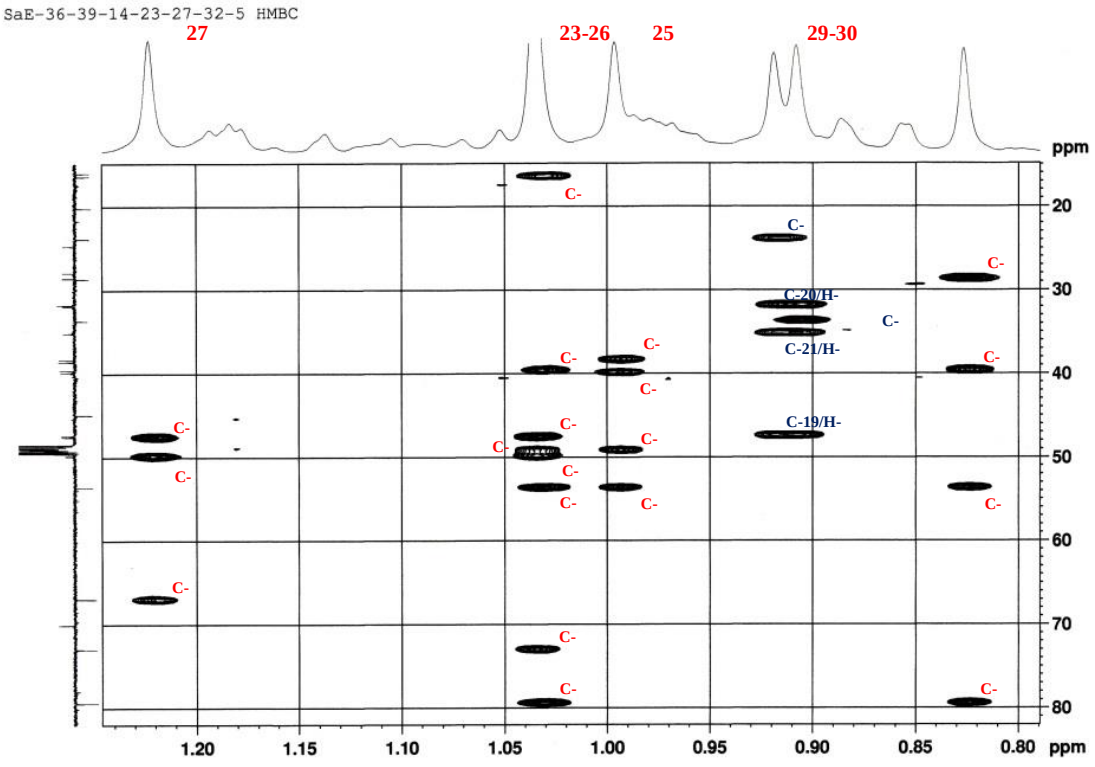
(Olean-12-ene-3β, 7β, 15α, 28β-tetraol)



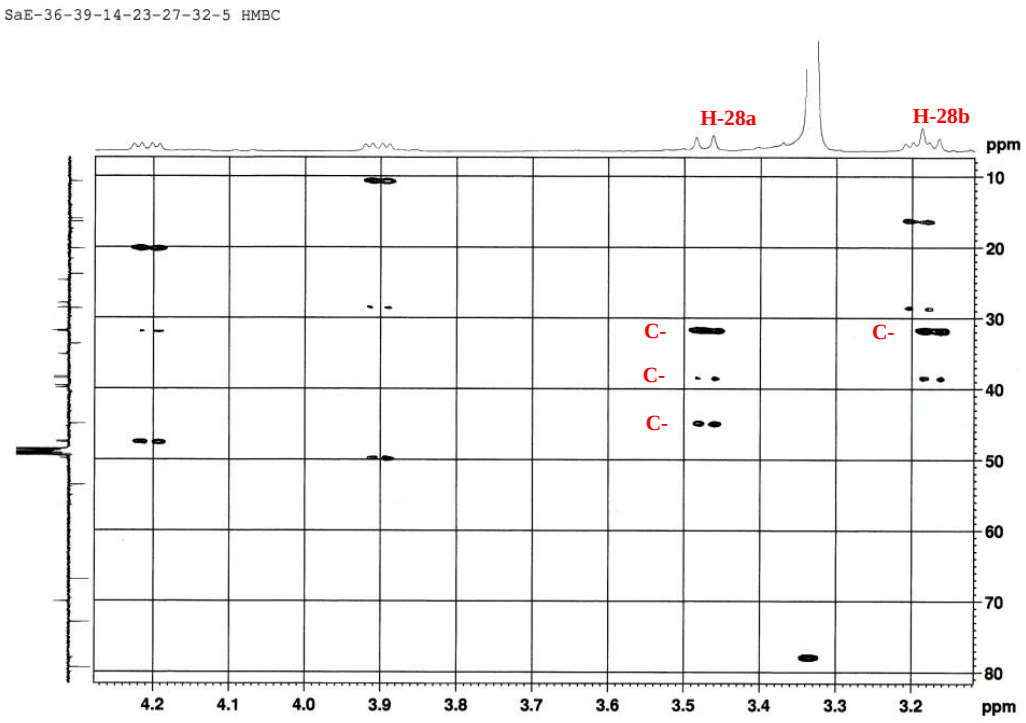
S64: ^{1}H-NMR (500 MHz, CD_3OD) Spectrum of Compound **10**



S65: ^{13}C-NMR J- mode (125 MHz, CD_3OD) Spectrum of Compound **10**



S66: HMBC (500 MHz) Spectrum of Compound **10** (From 15 to 82 ppm)



S67: HMBC (500 MHz) Spectrum of Compound **10** (From 8 to 81 ppm)