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Supporting Information

Xylogranatins F-R: Antifeedants from the Chinese Mangrove, *Xylocarpus granatum*, Suggesting a New Biogenetic Pathway to Tetranortriterpenoids

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Structural elucidation of xylogranatins N-P (9-11)

Xylogranatin N (**9**) had the molecular formula of $C_{32}H_{40}O_{10}$ as revealed by HR-TOFMS (*m/z* 607.2531, calcd for [M + Na^+] 607.2519). The NMR data of **9** were similar to those of xylogranatin I (**4**), except for the presence of one more 2-methylbutyryl group [d_H 0.86 (t, *J* = 7.4 Hz), 1.13 (d, *J* = 7.0 Hz), 1.50, m, 1.65, m, 2.38, m; d_C 11.9, q, 17.1, q, 27.9, t, 42.8, d, 177.8, s], deduced from ^{1}H-^{1}H COSY and HMBC correlations. The HMBC crosspeak from H-3 (d_H 5.29, s) of xylogranatin N (**9**) to the carbonyl carbon of this 2-methylbutyryl group suggested that this acyloxy function was attached to C-3. Alkaline hydrolysis of xylogranatin N (**9**) with sodium methoxide, followed by *O*-acetylation and methyl ester formation yielded xylogranatin M (**8**) (Scheme 2). The relative and thus the absolute configuration of C-3 in the above two compounds was determined to be the same by the NOE interaction from H-3 to H-5. Based on the result that the literature α_D value of (*R)*-2-methylbutanoic acid is negative (-14.3)[1] and that of (*S)*-2-methylbutanoic acid is positive (+19.3, 18.9),[2,3] the absolute configuration at C-2 in the 2-methylbutyryl group isolated after the cleavage of **9** was determined to be *S* by the α_D value of its acid (+16). Thus, xylogranatin N (**9**) was identified as the 3-*O*-2*S*-methylbutyrate ester form of xylogranatin I (**4**).

The molecular formula of xylogranatin O (**10**) was established as $C_{32}H_{38}O_{10}$ by HR-TOFMS (*m/z* 605.2374, calcd for [M + Na^+] 605.2363). The NMR data of xylogranatin O (**10**) were similar to those of xylogranatin I (**4)**, except for the presence of one more tigloyl group [d_H 1.83 (d, *J* = 7.1 Hz), 1.85, s, 6.89 (q, *J* = 7.1 Hz); d_C 12.2, q, 14.5, q, 129.8, s, 139.2, d, 169.1, s], deduced from ^{1}H-^{1}H COSY and HMBC correlations. The HMBC cross-peak from H-3 (d_H 5.33, s) of xylogranatin O (**10**) to the carbonyl carbon of this tigloyl group suggested that it was attached to C-3. Alkaline hydrolysis of xylogranatin O (**10**) with sodium methoxide, followed by *O*-acetylation and methylation yielded xylogranatin M (**8**) (Scheme 2). The absolute configuration of C-3 in the above two compounds was determined to be the same by the NOE interaction from H-3 to H-5. In addition, the *E*-configuration of the double bond in the tigloyl group was determined by the NOE interaction observed in **10** from H-3′ to

[1] A. I. Meyers, G. Knaus, K. Kamata, *J. Am. Chem. Soc.* **1974**, *96*, 268–270.

[2] S. Brechbuhler, G. Büchi, G. Milne, *J. Org. Chem*. **1967**, *32*, 2641–2642.

[3] O. Korver, M. V. Gorkom, *Tetrahedron* **1974**, *30*, 4041–4048.

Me-4′, but not from H-3′ to Me-5′. Therefore, xylogranatin O (**10**) was identified as the 3-*O*-tiglate ester form of xylogranatin I (**4**).

Xylogranatin P (**11**) had a molecular formula of $C_{31}H_{38}O_{10}$ established by HR-TOFMS (*m/z* 593.2373, calcd for [M + Na^+] 593.2363). The NMR data of xylogranatin P (**11**) were similar to those of xylogranatin I (**4)**, except for the presence of an isobutyryl group (d_H 1.13 (d, J = 7.0 Hz), 1.17 (d, J = 7.0 Hz), 2.58, m; d_C 19.2, q, 19.4, q, 35.4, d, 178.3, s), deduced from ^1H-^1H COSY and HMBC correlations. The HMBC cross peak from H-3 (d_H 5.29, s) of xylogranatin P (**11**) to the carbonyl carbon of this isobutyryl group suggested that it was attached to C-3. Alkaline hydrolysis of xylogranatin P (**11**) with sodium methoxide, followed by *O*-acetylation and methylation yielded xylogranatin M (**8**) (Scheme 2). The NOE interaction from H-3 to H-5 indicated that C-3 in **11** has the same relative (and thus absolute) configuration as C-3 in **8**. Based on the above results, xylogranatin P (**11**) was assigned as the 3-*O*-isobutyrate ester form of xylogranatin I (**4).**

Experimental details

***O*-Acetylation of xylogranatin F (1) to give xylogranatin G (2).** Xylogranatin F (**1**, 2 mg) was treated with acetic anhydride (100 µL) and pyridine (0.5 mL) at room temperature for 12 h, and then concentrated under reduced pressure to afford xylogranatin G (**2**, 1.8 mg), which was identified on the basis of its ^{1}H NMR and MS spectra.

Hydrogenation of xylogranatin F (1) to give xylogranatin H (3). To a solution of xylogranatin F (**1**, 4 mg) in ethanol (4 mL) 10% Pd/C (25 mg) was added, and the mixture was stirred for 4 h at room temperature under an atmosphere of H_2. Then the reaction mixture was filtered and concentrated under reduced pressure. The residue obtained was purified by C_{18}-RP HPLC aqueous acetonitrile to give xylogranatin H (**3**, 1.2 mg), which was identified on the basis of its ^{1}H NMR and MS spectra.

Chemical conversion of xylogranatin I (4) to give xylogranatin J (5): 30% aq. HCl (0.5 mL) was added dropwise to a solution of xylogranatin I (**4**) (10 mg) in methanol (2 mL) at room temperature for 2d. After removal of the solvent under reduced pressure, the residue was purified by C_{18}-RP HPLC with aqueous acetonitrile to afford the major product xylogranatin J (**5**, 9 mg) and minor product **5¢**(0.5 mg) (see Figure S4), among which **5¢** was characterized as C-3-epi-**5** by the detailed NOE interactions studies (see Figure S6).

Methylation of xylogranatin K (6) to give xylogranatin J (5): Xylogranatin K (**6**, 3 mg) was treated with excess $TMSCHN_2$ (0.5 mL) in a mixture of anhydrous *n*-hexane and methanol (1:1, 1mL) and stirred at room temperature over night to give xylogranatin J (**5**, 2.5 mg), which was identified on the basis of its ^{1}H NMR and MS spectra.

Chemical conversion of xylogranatin I (4) to give xylogranatin M (8): Xylogranatin I (**4**, 4 mg) was treated with acetic anhydride (200 µL) and pyridine (1 mL) at room temperature for 12 h. After removal of the solvent under reduced pressure, the residue was treated with excess $TMSCHN_2$ (0.5 mL) in the mixture of anhydrous *n*-hexane and methanol (1:1, 1 mL) and stirred at room temperature over night to afford xylogranatin M (**8**, 2.5 mg), which was identified on the basis of its ^{1}H NMR and MS spectra.

Chemical conversion of xylogranatin I (4) to give xylogranatins L (7): Xylogranatin I (**4**, 3 mg) was treated with 5% sodium hydride in dichloromethane (1 mL) and bromoethane (1 mL) at room temperature for 12 h. After removal of the solvent under reduced pressure, the residue was purified by

C_{18}-RP HPLC with aqueous acetonitrile to give xylogranatin L (**7**, 0.8 mg), which was identified on the basis of its ^{1}H NMR and MS spectra.

Chemical conversion of xylogranatins N-P (9-11) to give xylogranatin M (8): Xylogranatin N (**9**, 3 mg) was treated with 6% sodium methoxide in aqueous dioxane (1 mL) and refluxed for 8 h. The reaction mixture was neutralized with AG 50W-X8 (BIO-RAD, H^+ form) and partitioned between ethyl acetate and water (3:1). Then the organic phase was concentrated and treated with acetic anhydride (100 μL) and pyridine (0.5 mL) at room temperature for 12 h. After removal of the solvent under reduced pressure, the residue was further treated with excess $TMSCHN_2$ (0.5 mL) in the mixture of anhydrous *n*-hexane and methanol (1:1, 1mL) and stirred at room temperature over night. Then, the residue was purified by C_{18}-RP HPLC with aqueous acetonitrile to afford xylogranatin M (**8**, 1 mg), which was identified on the basis of its ^{1}H NMR and MS spectra. By the same method, each of xylogranatins O and P (**10** and **11**) yielded xylogranatin M.

Characterization of the absolute configuration of C-2 in the 2-methylbutyryl group of xylogranatin N (9): A portion of xylogranatin N (**9**, 3 mg) was dissolved in ethanol (0.5 mL), treated with 6% KOH in H_2O (1 mL) and stirred at room temperature for 24 h. The reaction mixture was concentrated and partitioned between ethyl acetate and water (3:1). Then, the ethyl acetate extract was analyzed by HPLC (see Figures S11a-c). After extracted with ethyl acetate for three times, the aqueous layer was acidified with concentrated hydrochloric acid until pH 3.0 and extracted again with dichloromethane for three times. The organic layer was combined, purified by Sephadex LH-20 CC (CH_2Cl_2 : CH_3OH 1:1) and dried over anhydrous Na_2SO_4 to provide 2-methylbutanoic acid (0.3 mg), which was identified on the basis of its MS spectrum. The absolute configuration at C-2 in 2-methylbutanoic acid was determined to be *S* by its α_D value ($[\alpha]^{25}_D$ +16 (*c* 0.03, EtOH)).

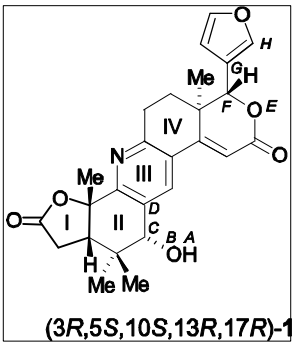
5℃: Amorphous powder; ^{1}H NMR ($CDCl_3$) *d* 7.54 (br s, H-21), 7.43 (br s, H-23), 6.86 (s, H-30), 6.48 (br s, H-22), 6.39 (s, H-15), 5.32 (s, H-17), 3.87 (d, 1.7 Hz, H-3), 3.72 (s, 7-OMe), 3.65 (s, 9-OMe), 3.63 (s, 3-OMe), 2.60 (m, H-10), 2.58 (dd, *J* = 16.8, 10.0 Hz, H-6a), 2.37 (m, H-11a), 2.34 (dd, *J* = 16.8, 4.0 Hz, H-6b), 2.22 (m, H-11b), 2.35 (m, H-5), 2.38 (m, H-12a), 1.96 (m, H-12b), 1.29 (d, *J* = 6.8 Hz, 3H, H_3-19), 1.27 (s, 3H, H_3-18), 1.06 (s, 3H, H_3-28), 0.78 (s, 3H, H_3-29); ESI-MS *m/z*: 497 [M - CH_3OH + H^+], 529 [M + H^+], 551 [M + Na^+], 567 [M + K^+].

Considerations on the occurrence of the new compounds as genuine natural products: By detailed HPLC analysis for the EtOAc extracts of four samples of the fresh seeds of *Xylocarpus granatum* (collected in October, and November 2005 and in January, and March 2006), we found that the chemical components and their concentrations varied with the seasons (see Figures S9a-d). These HPLC chromatograms clearly evidenced that xylogranatins F-K, M-Q are genuine natural products. In the fresh seeds sample collected in October (see Figure S9a), xylogranatins containing a pyridine ring (the first of the two subclasses) were the major components, with **2** as the main compound. As **2** was found to be very stable in chloroform, acetone, and various alcohol solvents, a transformation of **2** to **1** by an S_N1 reaction at C-3 at room temperature could be excluded. In the other fresh seeds samples (see Figures S9b-d), xylogranatins with a central furan core (i. e., belonging to the second subclass) were the dominating components and the content of **4**-**7** and **11**-**12** was relatively high. Xylogranatins **8**-**11**, i. e., the 3-*O*-acyl analogs of **4**, were stable in alcoholic solvents, the conversion of these compounds to **4** through an S_N1 reaction at C-3 (at room temperature) did not occur. Compound **4** was also stable in methanol and ethanol, but it could be transformed into **5** in methanol in the presence of a strong acid (see Figure S4), such as 30-50% hydrochloric acid or sulfuric acid. Its conversion into **7** in ethanol, however, was not observed under the same acidic conditions (see Figure S10). Generally, the automatic transformation into compounds **5**-**7** and **12** through S_N1 reaction at C-3 at room temperature in alcohol without the presence of a strong acid did not occur in our experiments. Furthermore, xylogranatin R was stable in various solvents used in the CC and NMR recording experiments. The above analysis again confirmed that xylogranatins F-K, M-Q are genuine natural products. Although the conversion of xylogranatin I (**4**) to xylogranatin L (**7**) was not observed in ethanol under acidic condition, we could not anticipate the same result for compound **4** when mixed with many other unknown compounds in the solvent of ethanol, just like in our extraction procedure. Whether xylogranatin L (**7**) is an authentic natural product or not will be clarified in future comparative extraction experiments on the same plant material with non-nucleophilic solvents.

Chemical conversion of **4** to **5** in methanol with a high concentration of hydrochloric acid with subsequent HPLC analysis (see Figure S4) coupled with ^{1}H NMR and NOE interaction studies (see Figures S5-S6) showed that the main product was xylogranatin J (**5)** (yield > 90%), i. e., with the same absolute configuration of *R* at C-3 as **4**, despite the intermediate cleavage at the C–O bond at C-3, hinting at a higher stability of the 3*a*-OH diastereomer of xylogranatins in a highly acidic solvent than the 3*b*-OH form. HPLC analysis coupled with ESI-MS studies showed that alkaline hydrolysis of xylogranatin N (**9)** with 6% KOH, gave 7-*O*-demethyl xylogranatin I (yield > 86%), and xylogranatin I (yield < 14%) as the products with a 3*a* C–O bond (see Figures S11a-c). The former was identified by its *O*-acetylation and then *O*-methylation to afford xylogranatin M (**8**). The latter was characterized by HPLC coelution with an authentic sample. In the above experiments, though the C–O bond at C-3 of xylogranatins was broken in acid or basic solvents, the major products were those with 3*a* C–O bond. This is possibly the reason for nature to produce these more stable diastereomers with *R* at C-3.

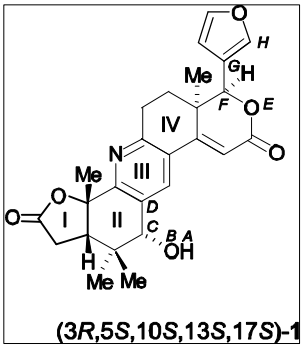
Xylogranatins C and D, also discovered in this study, are unusual 9,10-*seco* limonoids that have recently been isolated from the seeds of *X. granatum.* By detailed HPLC analysis, we had found that xylogranatin D was not a natural product as stated in the reference, but an artifact derived from the spontaneous rearrangement of xylogranatin C at room temperature in alcohol as solvent,e. g. when xylogranatin C was stored in methanol at room temperature for several days (see Figures S8a-c). The yield of xylogranatin D increased within several days. This was deduced from the HPLC analysis of the same xylogranatin C sample detected at the same wavelength of 220 nm one or two weeks after its HPLC preparation (see Figures S8a-c). In the above experiments, xylogranatins C and D were purified by C_{18} HPLC preparation and their structures were identified on the basis of their ^{1}H, ^{13}C NMR, and MS spectra.

Table S1. The conformers of (3*R*,5*S*,10*S*,13*R*,17*R*)-**1** found within a B3LYP conformational analysis.



Conformer	angle ABCD (°)	angle EFGH (°)	ring IV	energy (Hartrees)	rel. energy (kcal mol^{-1})
(R)-**1**_con1	47.5	22.6	pseudo-twist	-1513.11551	0.00
(R)-**1**_con2	166.3	22.5	pseudo-twist	-1513.11544	0.04
(R)-**1**_con3	48.0	-137.0	pseudo-twist	-1513.11548	0.02
(R)-**1**_con4	166.3	-138.3	pseudo-twist	-1513.11543	0.05
(R)-**1**_con5	47.5	-134.6	boat	-1513.11110	2.77
(R)-**1**_con6	166.6	29.7	boat	-1513.11088	2.90

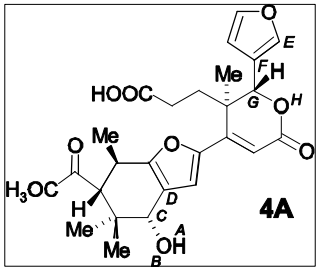
Table S2. The conformers of (3*R*,5*S*,10*S*,13*S*,17*S*)-**1** found within a B3LYP conformational analysis.



Conformer	angle	angle	ring IV	energy	rel. energy

	ABCD (°)	EFGH (°)		(Hartrees)	(kcal mol^{-1})
(S)-**1**_con1	40.4	137.9	pseudo-twist	-1513.1154987	0.10
(S)-**1**_con2	-168.1	138.1	pseudo-twist	-1513.1155548	0.07
(S)-**1**_con3	40.0	-65.7	pseudo-twist	-1513.1155792	0.05
(S)-**1**_con4	-168.0	-65.8	pseudo-twist	-1513.1156611	0.00

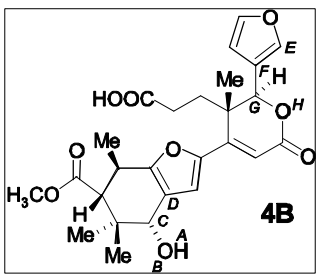
Table S3. The conformers of **4A** found within a B3LYP conformational analysis.



Conformer	angle ABCD (°)	angle EFGH (°)	rel. config.	energy (Hartrees)	rel. energy (kcal mol^{-1})
4A_conf1	-34.6	20.9	s-*cis*	-1725.11868	2.59
4A_conf2	-37.5	-136.9	s-*cis*	-1725.11803	3.00
4A_conf3	47.8	21.0	s-*cis*	-1725.11937	2.16
4A_conf4	164.5	20.9	s-*cis*	-1725.11913	2.13
4A_conf5	47.9	-143.5	s-*cis*	-1725.11868	2.59
4A_conf6	165.1	-136.4	s-*cis*	-1725.11863	2.62
4A_conf7	-57.0	21.1	s-*trans*	-1725.11857	2.66
4A_conf8	-41.7	-135.0	s-*trans*	-1725.11956	2.04
4A_conf9	54.8	24.2	s-*trans*	-1725.12072	1.32

4A_conf10	161.9	18.3	s-*trans*	-1725.12281	0.00
4A_conf11	54.0	-136.4	s-*trans*	-1725.12066	1.35
4A_conf12	161.7	-149.9	s-*trans*	-1725.12200	0.51

Table S4. The conformers of **4B** found within a B3LYP conformational analysis.



Conformer	angle	angle	rel. config.	energy	rel. energy

	ABCD (°)	EFGH (°)		(Hartrees)	(kcal mol^{-1})
4B_conf1	-36.8	109.9	s-*cis*	-1725.118322	0.36
4B_conf2	-37.0	-65.9	s-*cis*	-1725.116795	1.32
4B_conf3	45.8	109.9	s-*cis*	-1725.118670	0.14
4B_conf4	165.4	110.0	s-*cis*	-1725.118368	0.33
4B_conf5	46.1	-65.7	s-*cis*	-1725.117159	1.09
4B_conf6	165.4	-65.7	s-*cis*	-1725.116886	1.26
4B_conf7	-35.9	108.3	s-*trans*	-1725.118439	0.28
4B_conf8	.36.1	-75.5	s-*trans*	-1725.117134	1.10
4B_conf9	46.6	108.1	s-*trans*	-1725.118893	0.00
4B_conf10	164.9	107.8	s-*trans*	-1725.118854	0.02
4B_conf11	46.8	-75.6	s-*trans*	-1725.117564	0.83
4B_conf12	165.0	-77.6	s-*trans*	-1725.117542	0.85

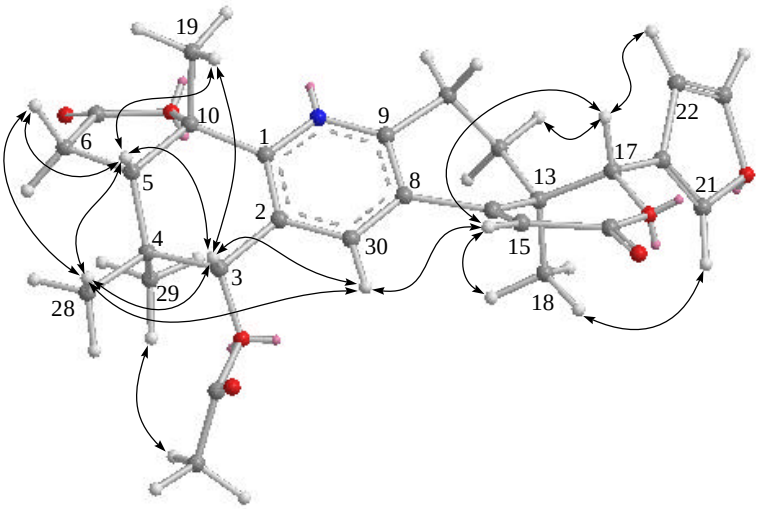


Figure S1. Significant NOE correlations for xylogranatin G (**2**).

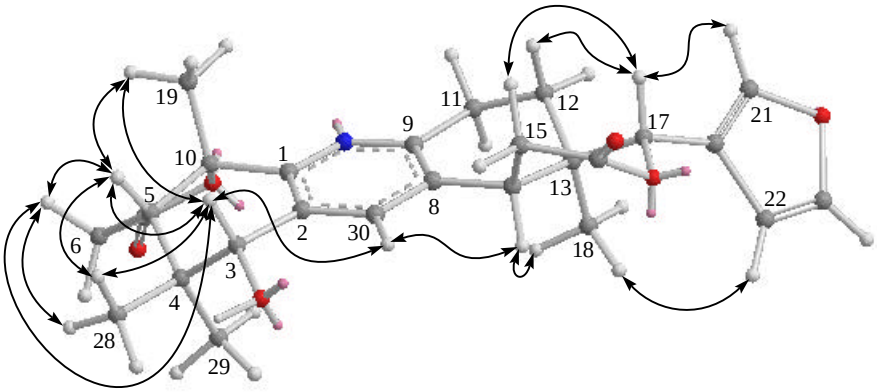


Figure S2. Significant NOE correlations for xylogranatin H (**3**).

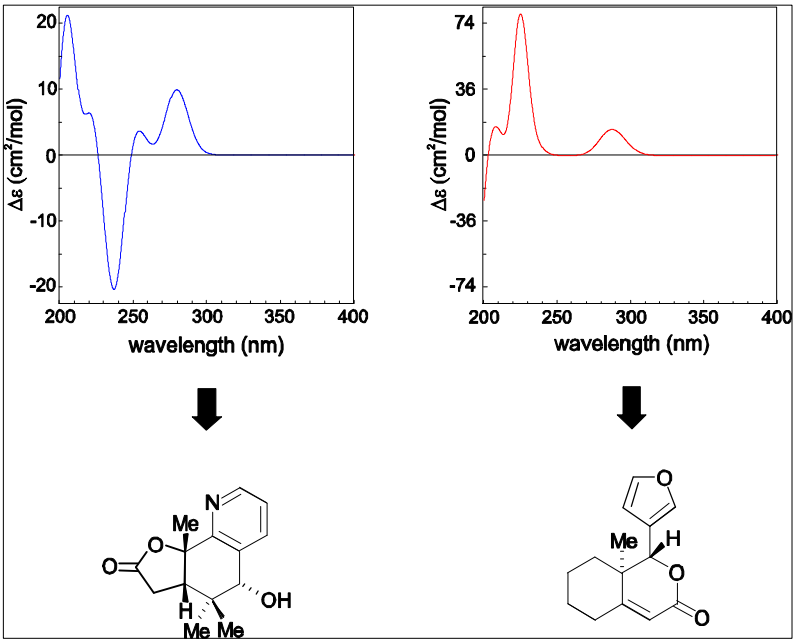
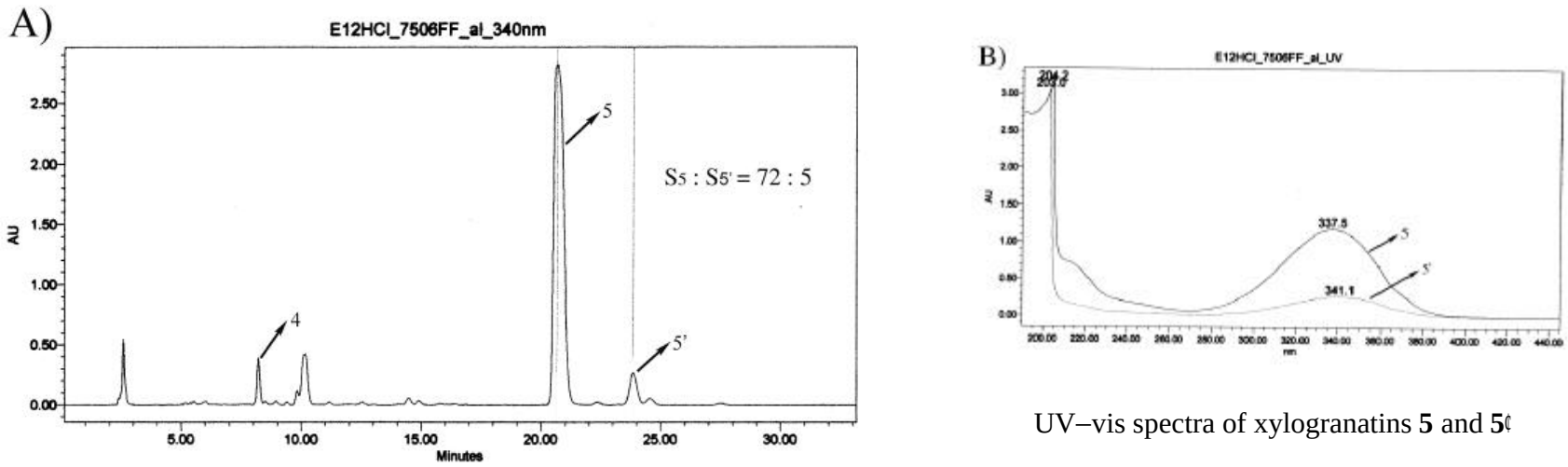


Figure S3. CD spectra (calculated with TD B3LYP/6-31G(d)) of the models of (3*R*,5*S*,10*S*,13*R*,17*R*)-**1**: Only the lower part results in a negative Cotton effect at 235 nm.

HPLC analysis for the products of treatment of **4** with 30% hydrochloric acid in methanol



UV−vis spectra of xylogranatins **5** and **5′**

Figure S4. The HPLC chromatogram of the reaction mixture using the solvent system named 7506FF (about 45% acetonitrile). The major product is **5** and the minor one is **5′**. The peak area ratio of **5** to **5′** is 72 to 5.

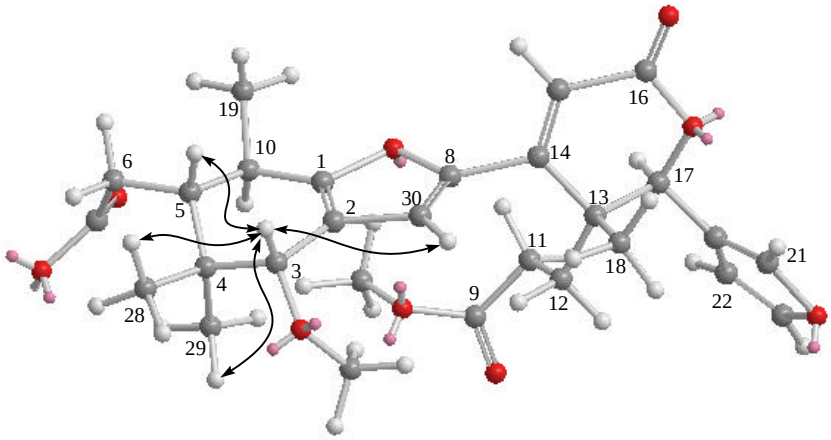


Figure S5. Significant NOE correlations for xylogranatin J (**5**).

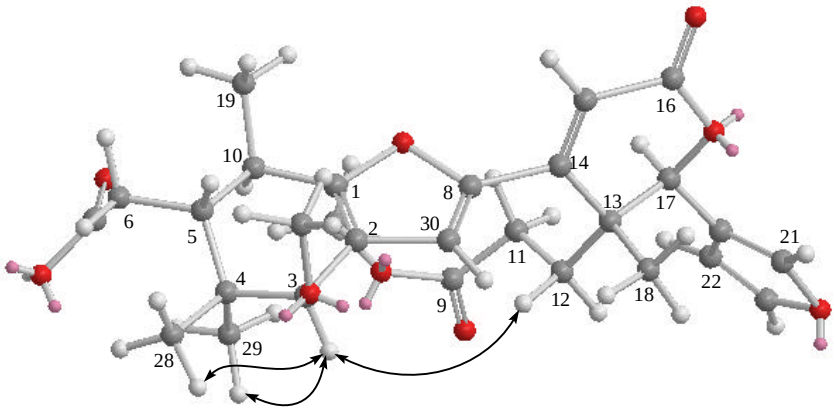


Figure S6. Significant NOE correlations for **5**.

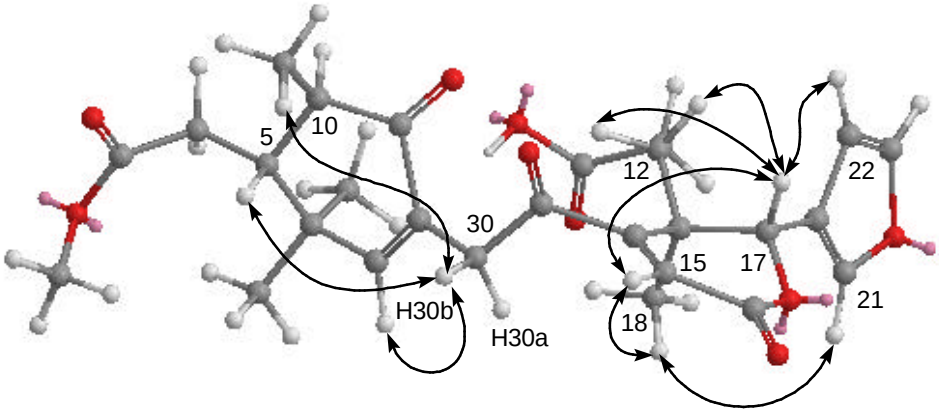


Figure S7. Significant NOE interactions for xylogranatin R(**13**)

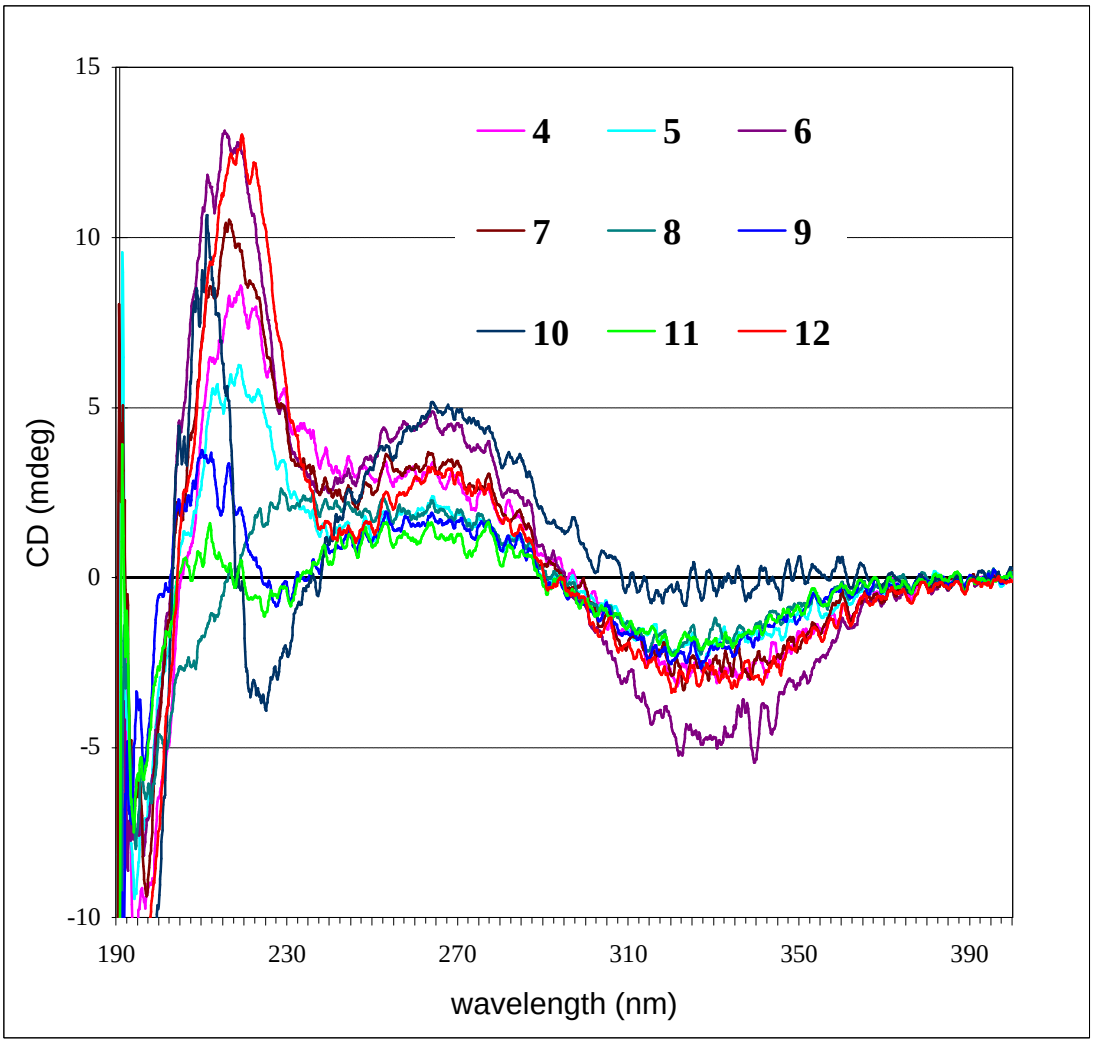
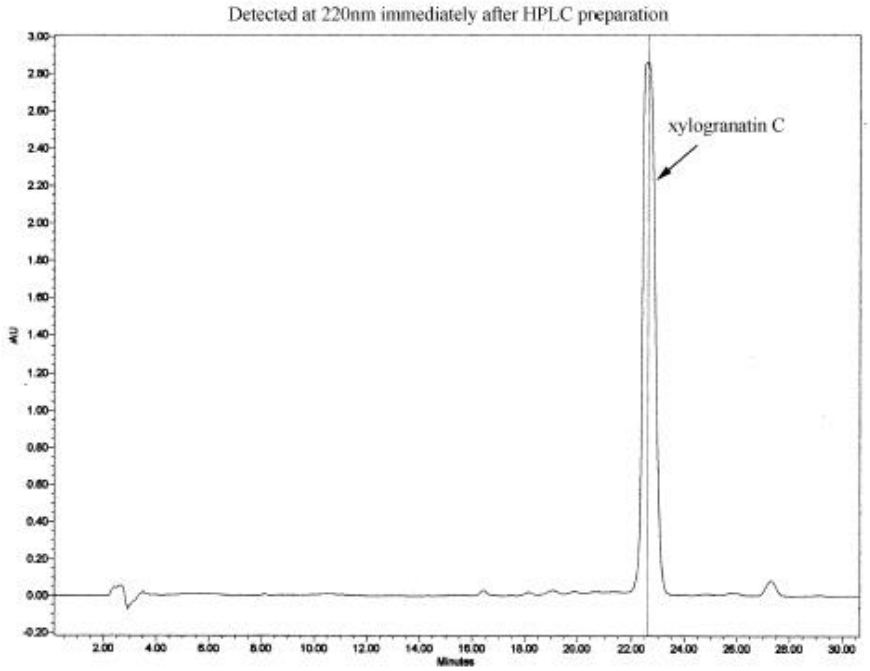
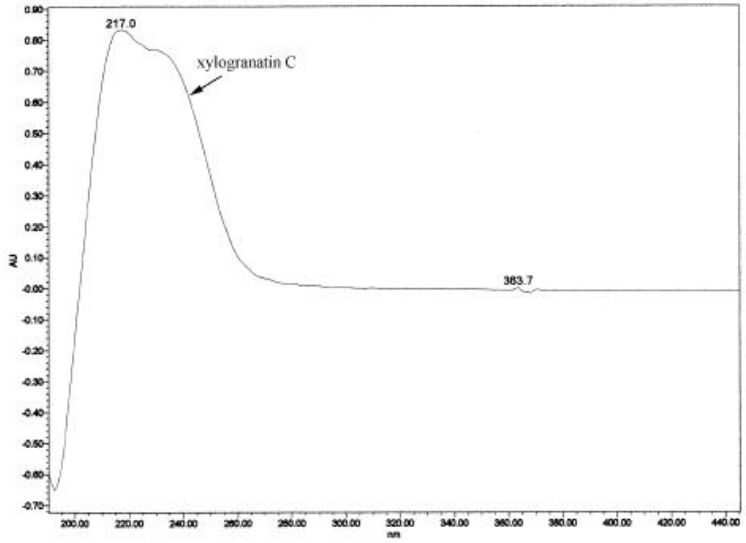


Figure S8. CD spectra of xylogranatins I-Q (**4**-**12**) in methanol.

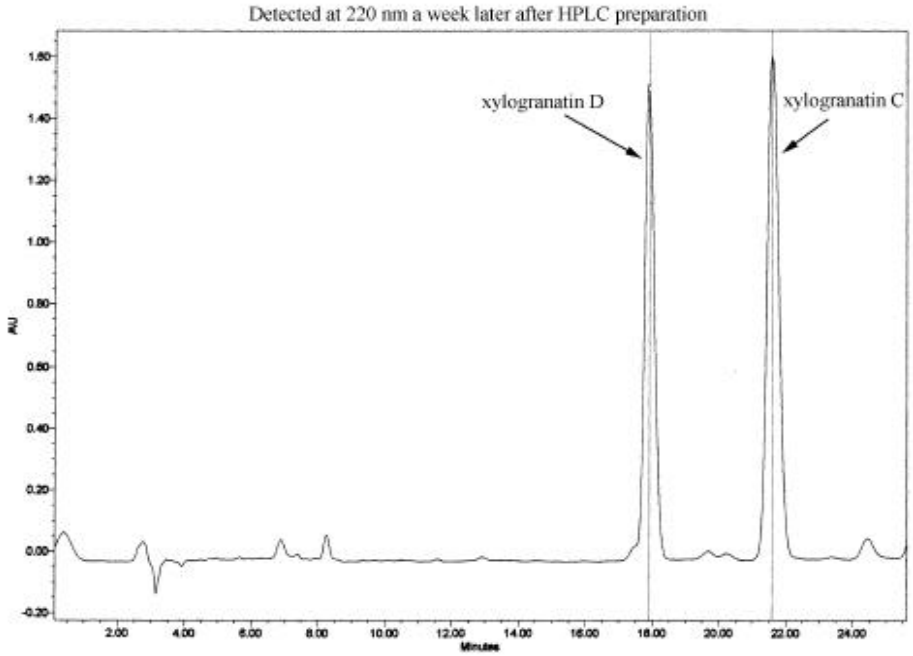
HPLC Analysis of xylogranatin C after its RP-HPLC preparation (**Figures S9a-c**)

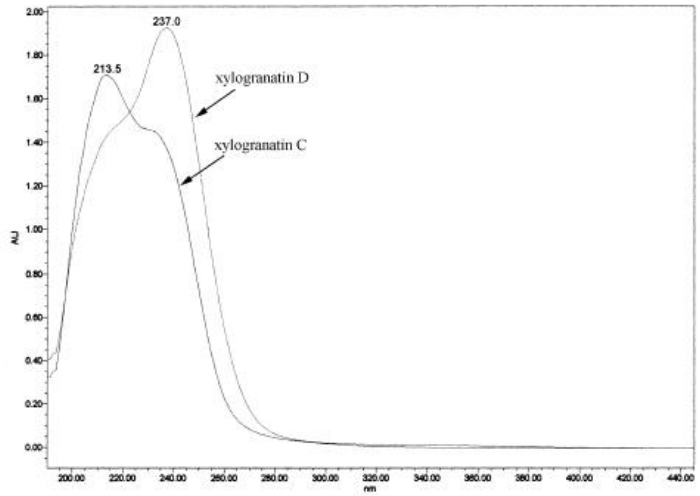




UV–vis spectrum of xylogranatin C

Figure S9a. Detected at 220 nm immediately after its RP-HPLC preparation (MeCN–Water 35:65).

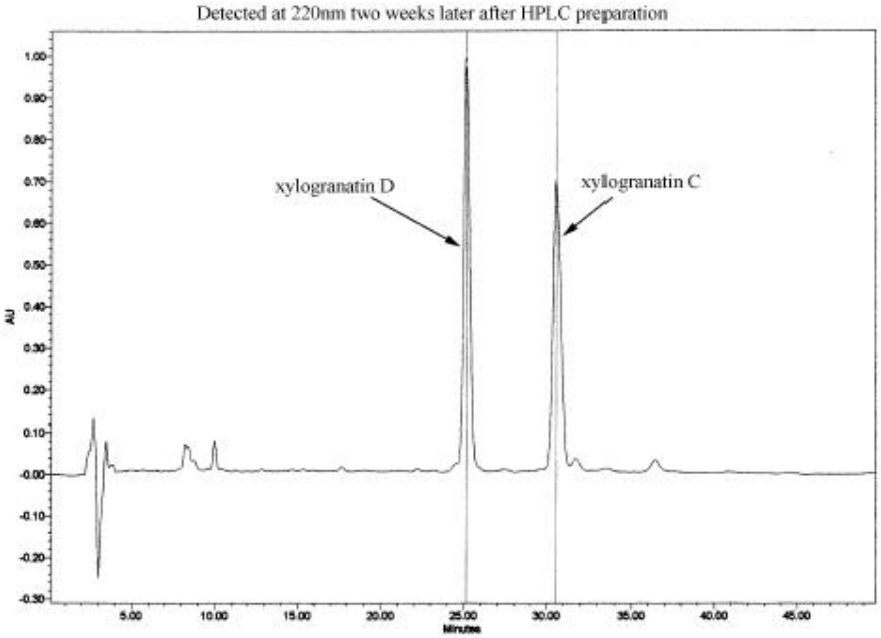


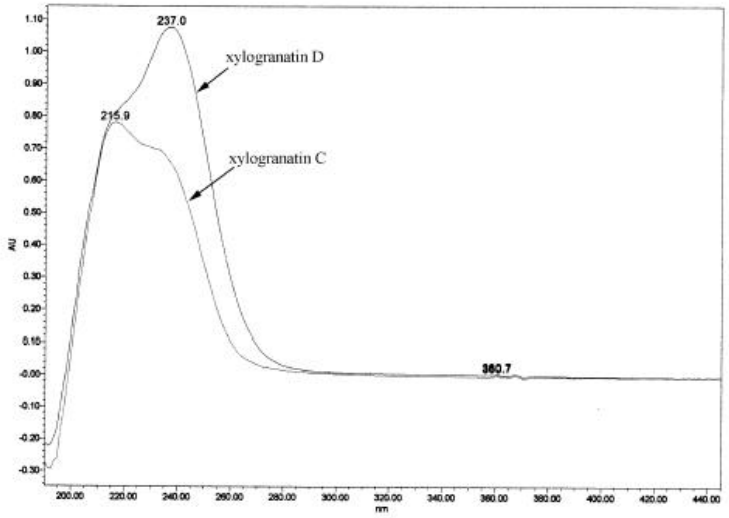


UV−vis spectra of xylogranatins C and D

Figure S9b. Detected at 220 nm a week after the day of its RP-HPLC preparation (MeCN−Water 35:65).

(xylogranatin C was stored in methanol at room temperature)





UV–vis spectra of xylogranatins C and D

Figure S9c. Detected at 220 nm two weeks after the day of its RP-HPLC Preparation.

(MeCN–Water 34:66) (xylogranatin C was stored in methanol at room temperature)

HPLC Analysis for the EtOAc extracts of four samples of fresh seeds of *Xylocarpus granatum* **(Figures S10a-d)**

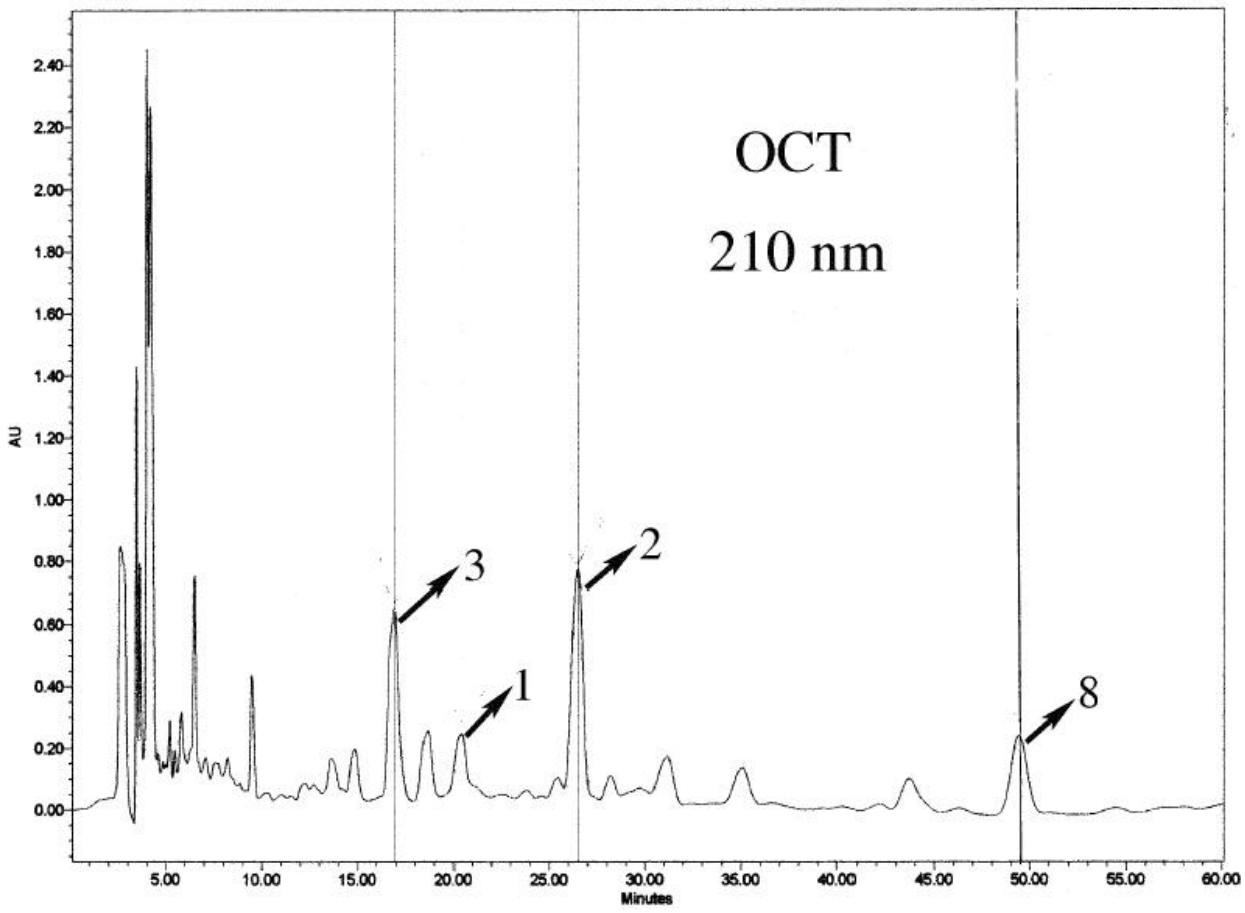


Figure S10a. The fresh seeds of *Xylocarpus granatum* collected in October, 2005 (detected at 210 nm).

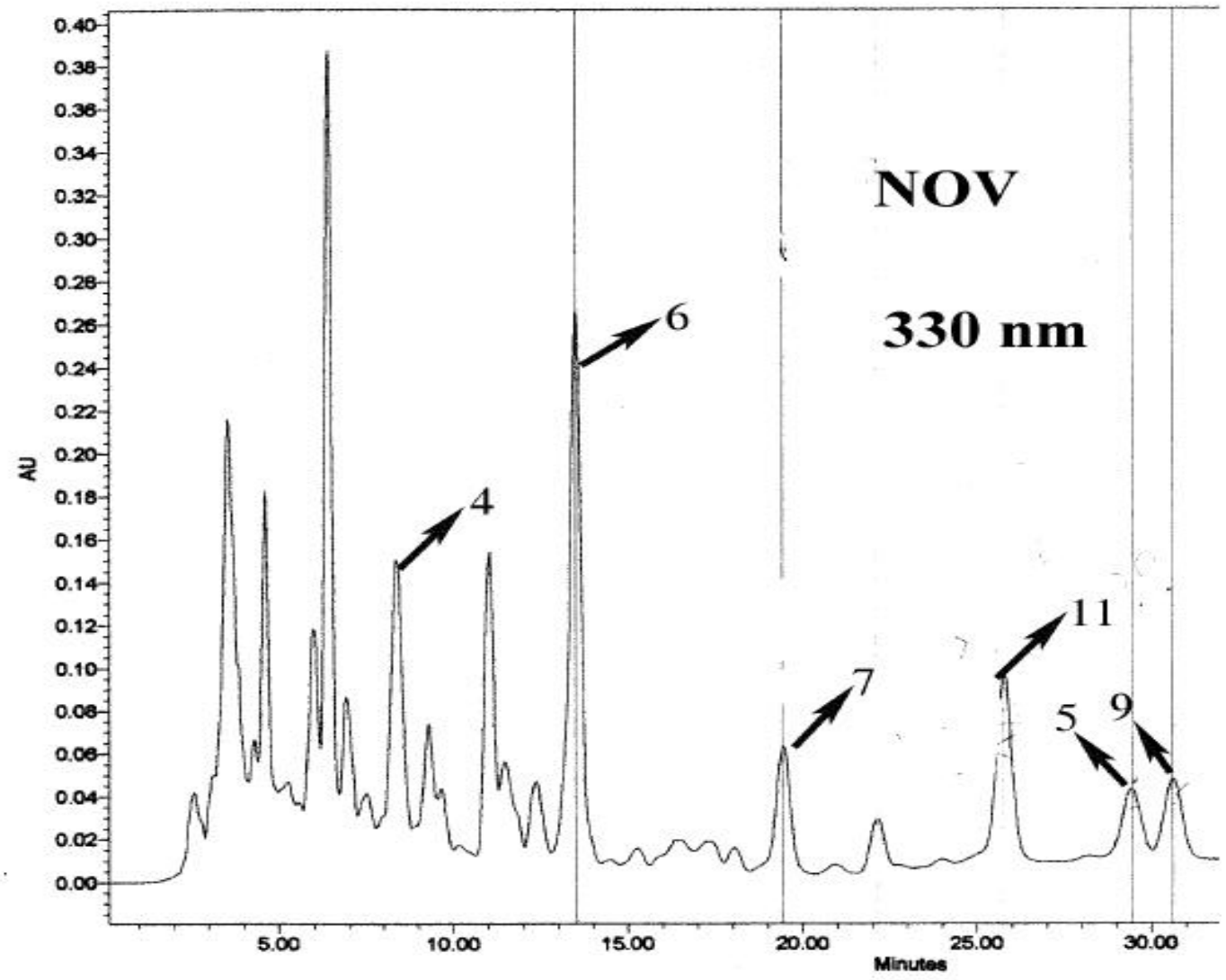


Figure S10b. The fresh seeds of *Xylocarpus granatum* collected in November, 2005 (detected at 330 nm).

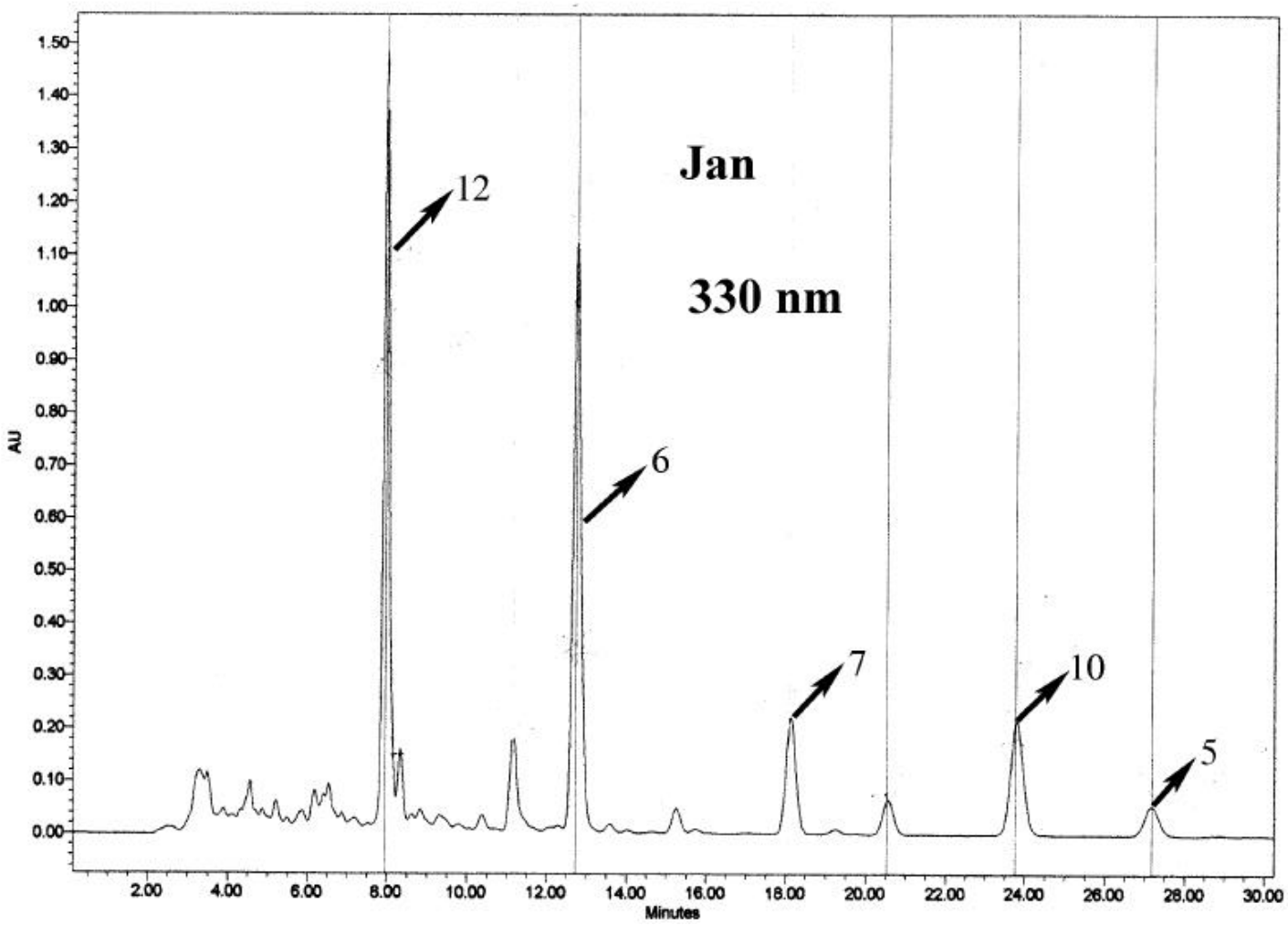


Figure S10c**.** The fresh seeds of *Xylocarpus granatum* collected in January, 2006 (detected at 330 nm).

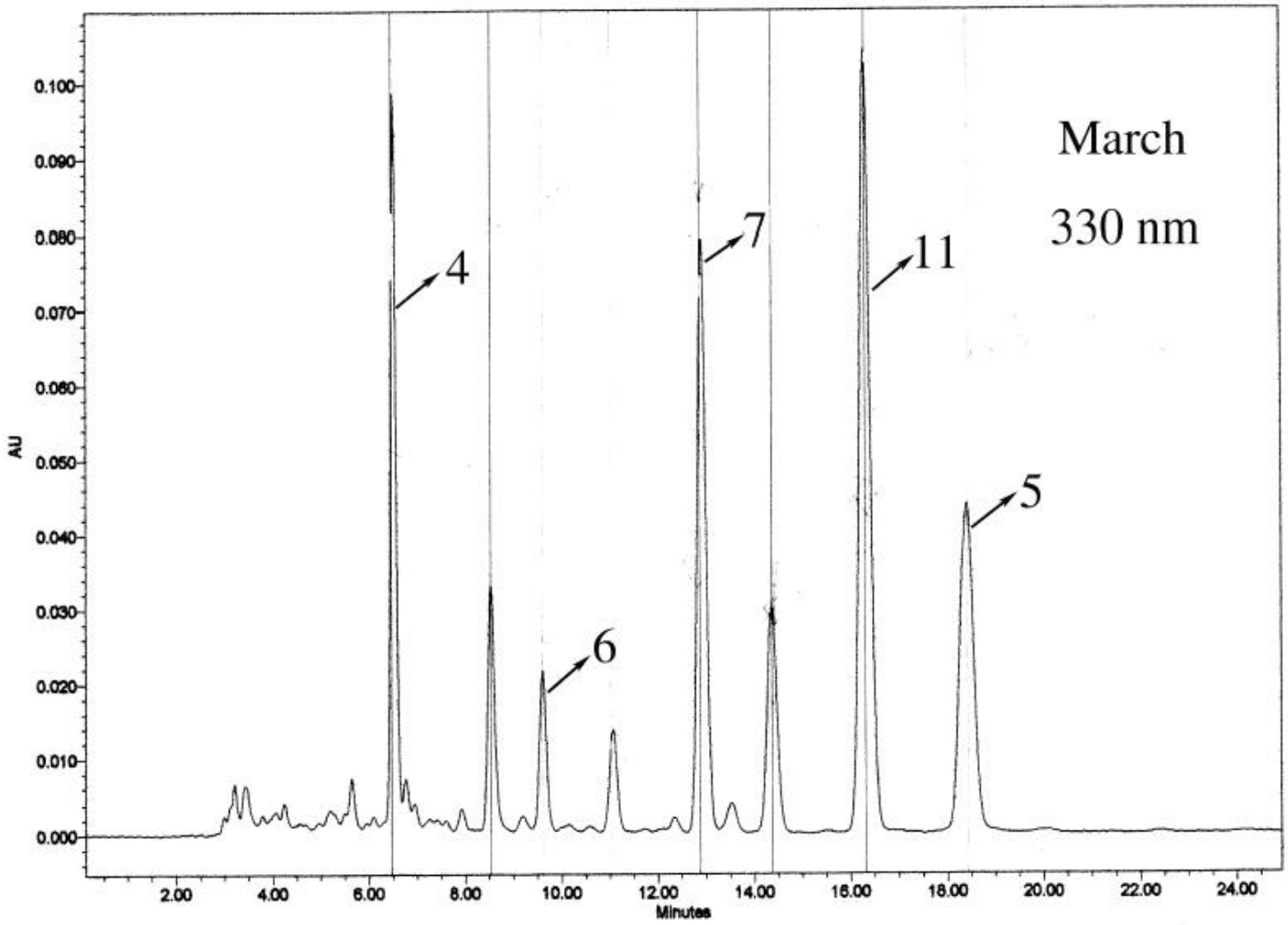
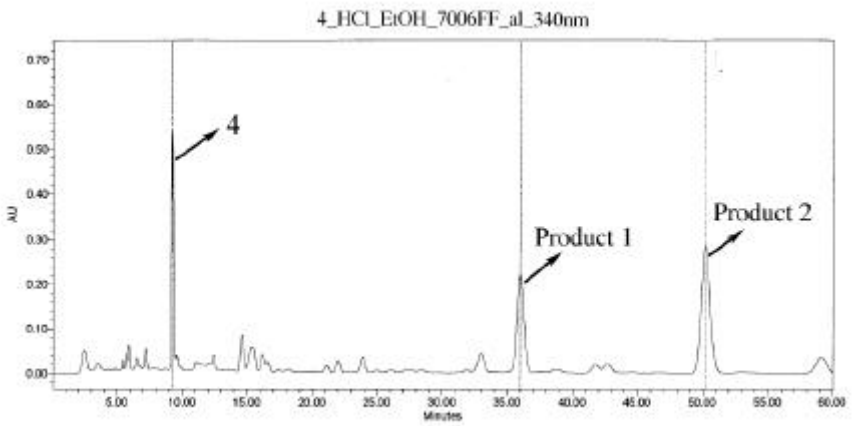
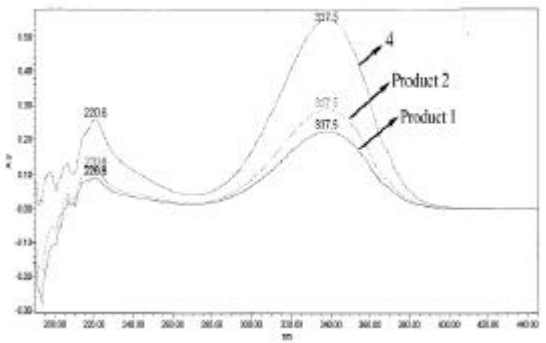


Figure S10d. The fresh seeds of *Xylocarpus granatum* collected in March, 2006 (detected at 330 nm)

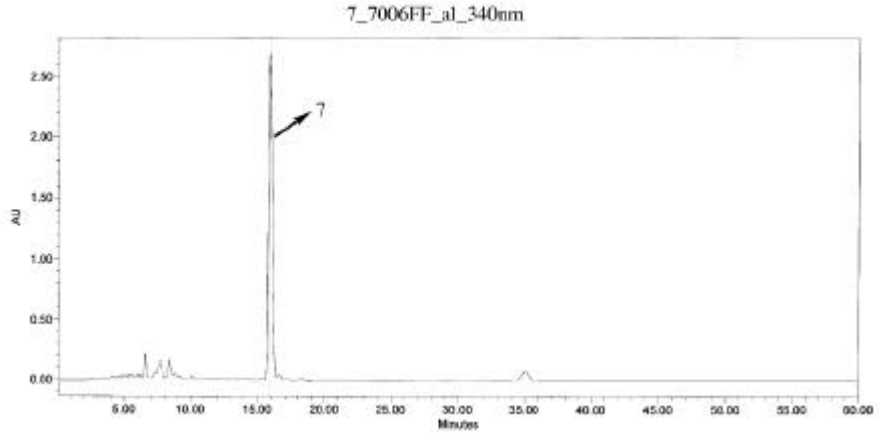
HPLC analysis of the products of treatment of xylogranatin I (**4**) with 30% hydrochloric acid in ethanol



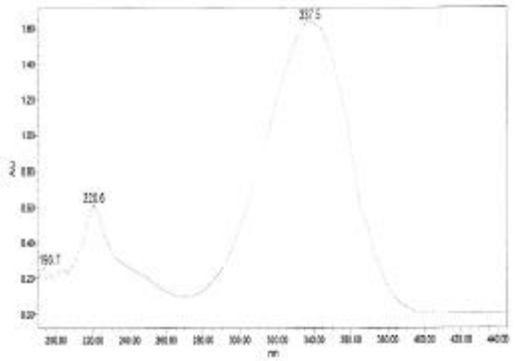
a)



UV−vis spectra of **4** and products **1** and **2**



b)



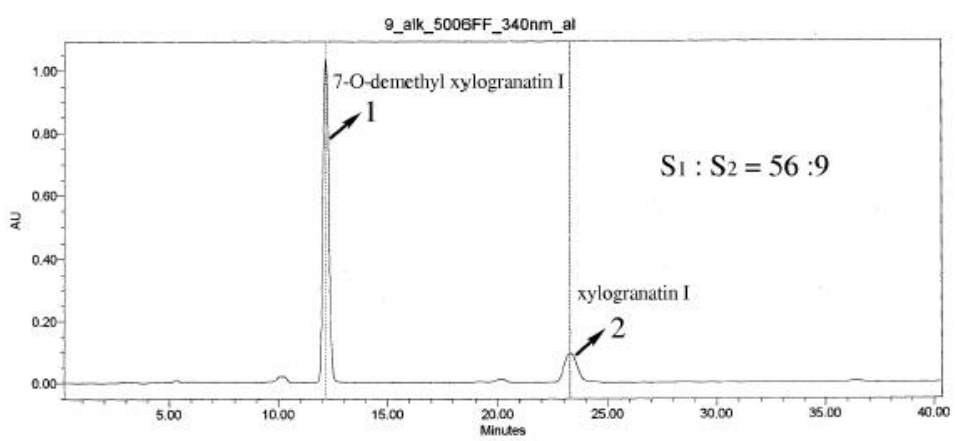
UV−vis spectra of 7

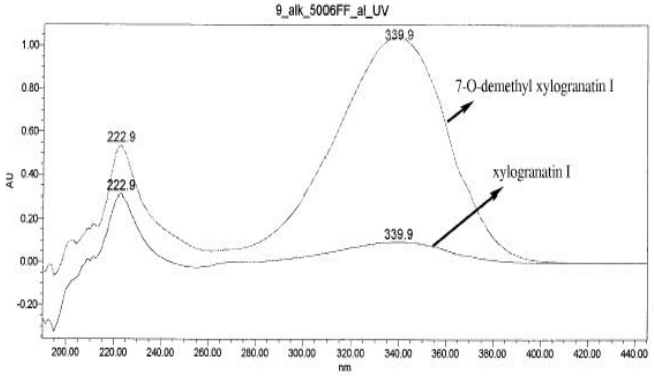
Figure S11. a) The HPLC chromatogram of the reaction mixture using the solvent system named 7006FF

b) The HPLC chromatogram of the standard **7** using the same solvent system (about 40% acetonitrile)

HPLC analysis for the products of **9** with 6% KOH in ethanol and water (1:2)

(Figures S11a-c)





UV−vis spectra

Figure S12a. The HPLC chromatogram of the reaction mixture using the solvent system named 5006FF (about 20% acetonitrile); the peak area ratio of **1** to **2** is 56 to 9.

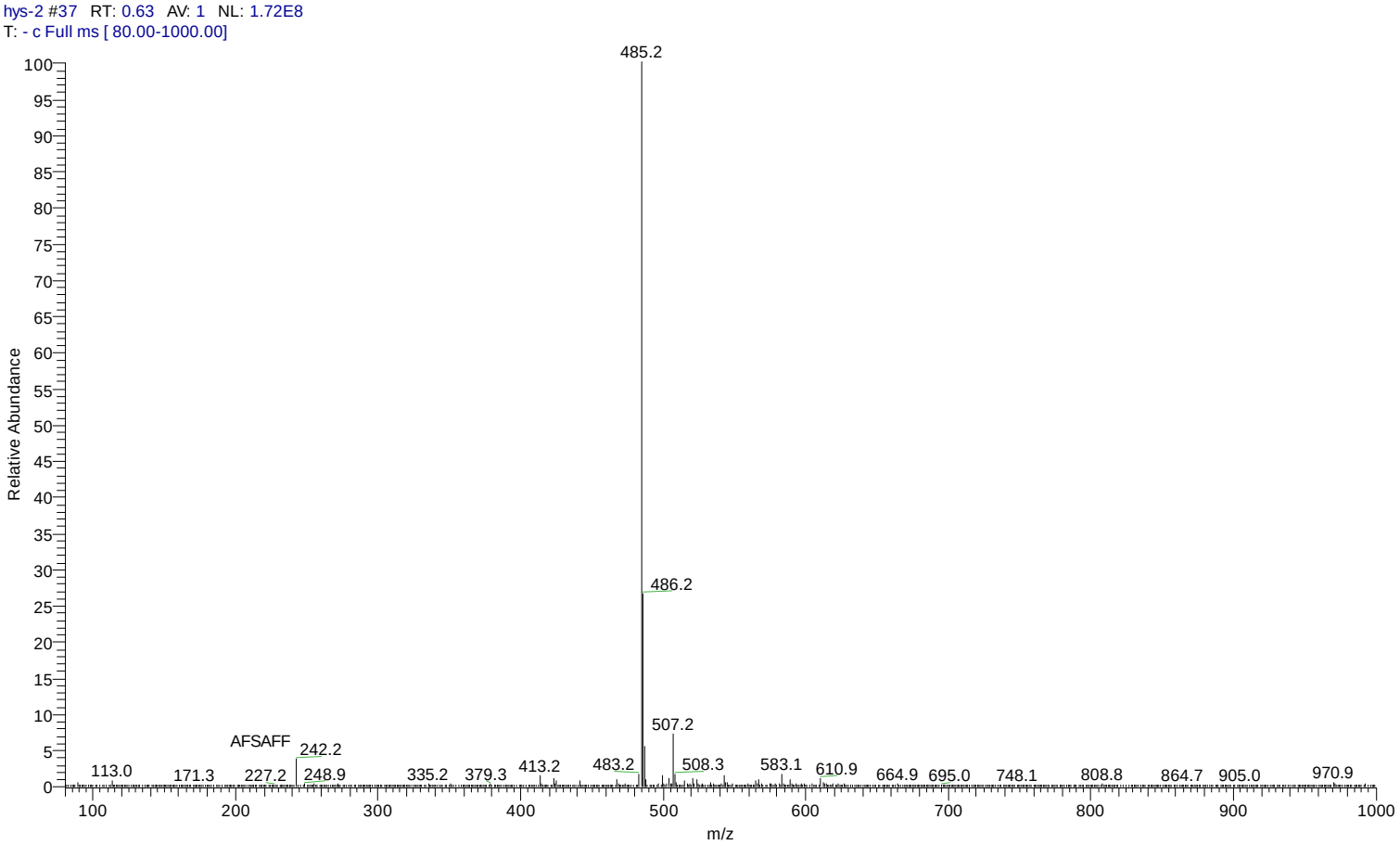


Figure S12b. ESI-MS of peak **1** (7-*O*-demethyl xylogranatin I) in the HPLC chromatogram of Figure S11a. (negative mode)

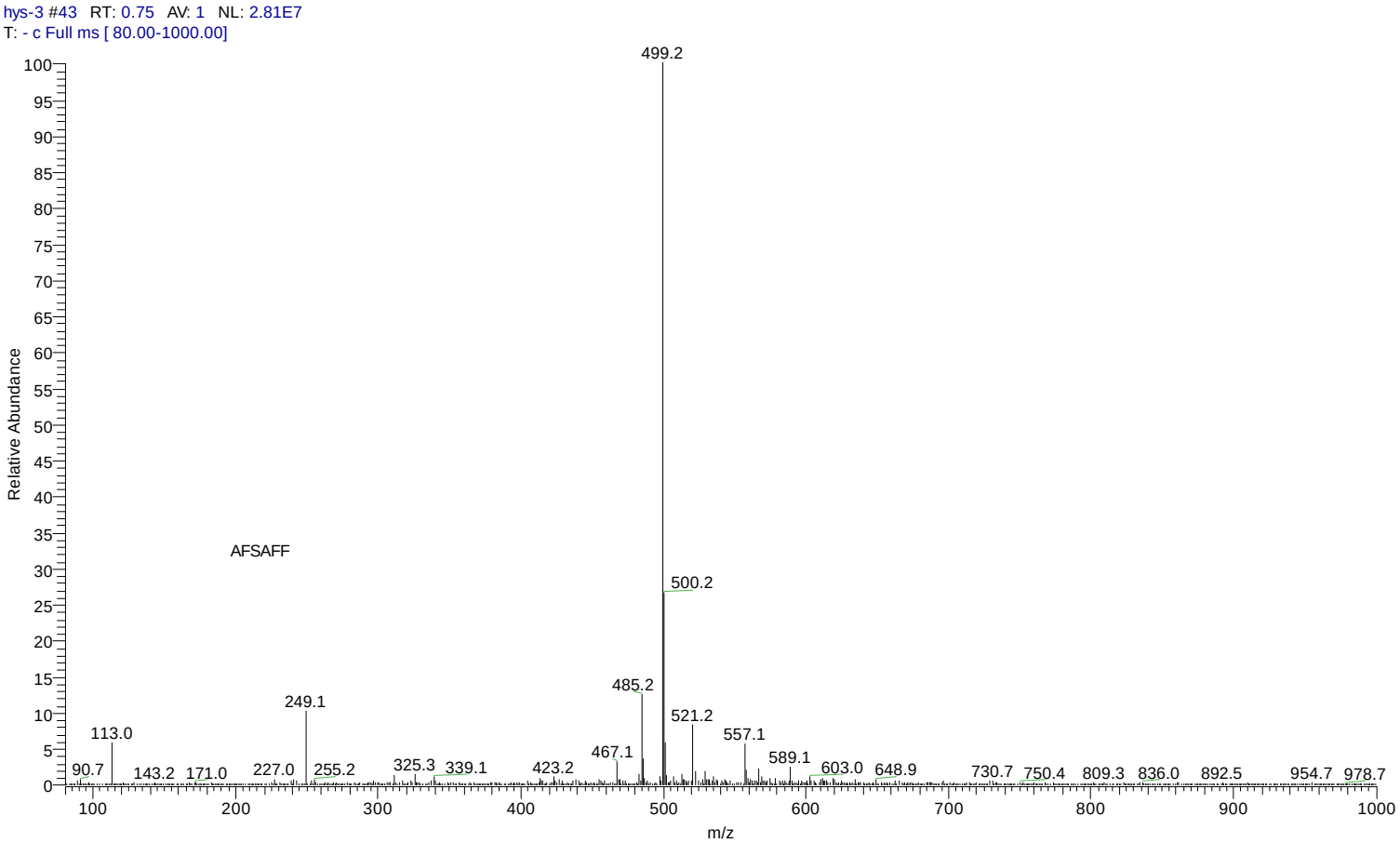


Figure S12c. ESI-MS of peak **2** (xylogranatin I) in the HPLC chromatogram of Figure S11a.

(negative mode)

Supporting Information-P

Xylogranatins F-R: Antifeedants from the Chinese Mangrove, *Xylocarpus granatum*, Suggesting a New Biogenetic Pathway to Tetranortriterpenoids

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wwujun2003@yahoo.com; bringman@chemie.uni-wuerzburg.de

Copies of MS, NMR spectra of **1-13, 1s, 1r, 3s, 3r, 4¢, 4¢s, 4¢ r and 5¢**.

For xylogranatin F (1), 1s and 1r (S10~S28)**:**

(1) IR spectrum of xylogranatin F

(2) HR-TOFMS of xylogranatin F

(3) ^{1}H NMR (500 MHz) Spectrum of xylogranatin F in $CDCl_3$

(4) ^{13}C NMR (125 MHz) Spectrum of xylogranatin F in $CDCl_3$

(5) DEPT 90° and 135°experiments of xylogranatin F in $CDCl_3$

(6) ^{1}H-^{1}H COSY Spectrum of xylogranatin F in $CDCl_3$

(7) HSQC Spectrum of xylogranatin F in $CDCl_3$

(8) A segment of HSQC Spectrum of xylogranatin F in $CDCl_3$

(9) HMBC Spectrum of xylogranatin F in $CDCl_3$

(10) A segment of NOESY Spectrum of xylogranatin F in $CDCl_3$

(11) A segment of NOESY Spectrum of xylogranatin F in $CDCl_3$

(12) A segment of NOESY Spectrum of xylogranatin F in $CDCl_3$

(13) A segment of NOESY Spectrum of xylogranatin F in $CDCl_3$

(14) ESI-MS of **1s**

(15) A Segment of ^{1}H NMR (500 MHz) of **1s** in $CDCl_3$

(16) A Segment of ^{1}H NMR (500 MHz) of **1s** in $CDCl_3$

(17) ESI-MS of **1r**

(18) A Segment of ^{1}H NMR (500 MHz) of **1r** in $CDCl_3$

(19) A Segment of ^{1}H NMR (500 MHz) of **1r** in $CDCl_3$

For xylogranatin G (2) (S29~S38)**:**

(1) IR spectrum of xylogranatin G

(2) TOFMS of xylogranatin G

(3) HR-TOFMS of xylogranatin G

(4) ^{1}H NMR (500 MHz) Spectrum of xylogranatin G in $CDCl_3$

(5) ^{13}C NMR (125 MHz) Spectrum and DEPT experiments of xylogranatin G in $CDCl_3$

(6) HSQC Spectrum of xylogranatin G in $CDCl_3$

(7) HMBC Spectrum of xylogranatin G in $CDCl_3$

(8) A Segment of NOESY Spectrum of xylogranatin G in $CDCl_3$

(9) A Segment of NOESY Spectrum of xylogranatin G in $CDCl_3$

(10) A Segment of NOESY Spectrum of xylogranatin G in $CDCl_3$

For xylogranatin H (3), 3s and 3r (S39~S55)**:**

(1) IR spectrum of xylogranatin H

(2) HR-TOFMS of xylogranatin H

(3) ^{1}H NMR (500 MHz) Spectrum of xylogranatin H in methanol-d_4

(4) ^{13}C NMR (125 MHz) Spectrum and DEPT experiments of xylogranatin H in methanol-d_4

(5) ^{1}H-^{1}H COSY Spectrum of xylogranatin H in methanol-d_4

(6) A Segment of ^{1}H-^{1}H COSY Spectrum of xylogranatin H in methanol-d_4

(7) HSQC Spectrum of xylogranatin H in methanol-d_4

(8) HMBC Spectrum of xylogranatin H in methanol-d_4

(9) NOESY Spectrum of xylogranatin H in methanol-d_4

(10) A Segment of NOESY Spectrum of xylogranatin H in methanol-d_4

(11) A Segment of NOESY Spectrum of xylogranatin H in methanol-d_4

(12) ESI-MS of **3s**

(13) ^{1}H NMR (500 MHz) of **3s** in methanol-d_4

(14) A Segment of ^{1}H NMR (500 MHz) of **3s** in methanol-d_4

(15) ESI-MS of **3r**

(16) ^{1}H NMR (500 MHz) of **3r** in methanol-d_4

(17) A Segment of ^{1}H NMR (500 MHz) of **3r** in methanol-d_4

For xylogranatin I (4), 4¢, 4¢s and 4¢r (S56~S77)**:**

(1) IR spectrum of xylogranatin I

(2) TOFMS of xylogranatin I

(3) HR-TOFMS of xylogranatin I

(4) ^{1}H NMR (500 MHz) Spectrum of xylogranatin I in methanol-d_4

(5) ^{13}C NMR (125 MHz) Spectrum and DEPT experiments of xylogranatin I in methanol-d_4

(6) A Segment of ^{1}H-^{1}H COSY Spectrum of xylogranatin I in methanol-d_4

(7) A Segment of ^{1}H-^{1}H COSY Spectrum of xylogranatin I in methanol-d_4

(8) HSQC Spectrum of xylogranatin I in methanol-d_4

(9) HMBC Spectrum of xylogranatin I in methanol-d_4

(10) A Segment of NOESY Spectrum of xylogranatin I in methanol-d_4

(11) A Segment of NOESY Spectrum of xylogranatin I in methanol-d_4

(12) A Segment of NOESY Spectrum of xylogranatin I in methanol-d_4

(13) A Segment of NOESY Spectrum of xylogranatin I in methanol-d_4

(14) ^{1}H NMR (500 MHz) Spectrum of **4¢** in $CDCl_3$

(15) ^{13}C NMR (125 MHz) Spectrum and DEPT experiments of **4¢** in $CDCl_3$

(16) A Segment of ^{13}C NMR (125 MHz) Spectrum and DEPT experiments of **4¢** in $CDCl_3$

(17) ESI-MS of **4¢s**

(18) ^{1}H NMR (500 MHz) of **4¢s** in methanol-d_4

(19) A Segment of ^{1}H NMR (500 MHz) of **4¢s** in methanol-d_4

(20) ESI-MS of **4¢r**

(21) ^{1}H NMR (500 MHz) of **4¢r** in methanol-d_4

(22) A Segment of ^{1}H NMR (500 MHz) of **4¢r** in methanol-d_4

For xylogranatin J (5) and 5¢ (S78~S94)**:**

(1) IR spectrum of xylogranatin J

(2) HR-TOFMS of xylogranatin J

(3) ^{1}H NMR (500 MHz) Spectrum of xylogranatin J in methanol-d_4

(4) ^{13}C NMR (125 MHz) Spectrum and DEPT experiments of xylogranatin J in methanol-d_4

(5) HSQC Spectrum of xylogranatin J in methanol-d_4

(6) HMBC Spectrum of xylogranatin J in methanol-d_4

(7) ^{1}H NMR (500 MHz) Spectrum of the Major Product **(5)** Detected in methanol-d_4

(8) ^{1}H NMR (500 MHz) Spectrum of the Major Product **(5)** Detected in $CDCl_3$

(9) ^{13}C NMR (125 MHz) Spectrum and DEPT experiments of the Major Product **(5)** Detected in $CDCl_3$

(10) NOESY Spectrum of the Major Product **(5)** Detected in $CDCl_3$

(11) A Segment of NOESY Spectrum of the Major Product **(5)** Detected in $CDCl_3$

(12) ESI-MS of the Minor Product **(5¢)**

(13) ^{1}H NMR (500 MHz) Spectrum of the Minor Product **(5¢)** Detected in $CDCl_3$

(14) A Segment of ^{1}H NMR (500 MHz) Spectrum of **5¢** Detected in $CDCl_3$

(15) A Segment of ^{1}H NMR (500 MHz) Spectrum of **5¢** Detected in $CDCl_3$

(16) NOESY Spectrum of **5¢** Detected in $CDCl_3$

(17) A Segment of NOESY Spectrum of **5¢** Detected in $CDCl_3$

For xylogranatin K (6) (S95~S102)**:**

(1) IR spectrum of xylogranatin K

(2) HR-TOFMS of xylogranatin K

(3) ^{1}H NMR (500 MHz) Spectrum of xylogranatin K in methanol-d_4

(4) ^{13}C NMR (125 MHz) Spectrum of xylogranatin K in methanol-d_4

(5) DEPT experiments of xylogranatin K in methanol-d_4

(6) HSQC Spectrum of xylogranatin K in methanol-d_4

(7) HMBC Spectrum of xylogranatin K in methanol-d_4

(8) A Segment of NOESY Spectrum of xylogranatin K in methanol-d_4

For xylogranatin L (7) (S103~S110)**:**

(1) IR spectrum of xylogranatin L

(2) HR-TOFMS of xylogranatin L

(3) ^{1}H NMR (500 MHz) Spectrum of xylogranatin L in methanol-d_4

(4) ^{13}C NMR (125 MHz) Spectrum of xylogranatin L in methanol-d_4

(5) DEPT experiments of xylogranatin L in methanol-d_4

(6) HSQC Spectrum of xylogranatin L in methanol-d_4

(7) HMBC Spectrum of xylogranatin L in methanol-d_4

(8) A Segment of NOESY Spectrum of xylogranatin L in methanol-d_4

For xylogranatin M (8) (S111~S117)**:**

(1) IR spectrum of xylogranatin M

(2) HR-TOFMS of xylogranatin M

(3) ^{1}H NMR (500 MHz) Spectrum of xylogranatin M in methanol-d_4

(4) ^{13}C NMR (125 MHz) Spectrum and DEPT experiments of xylogranatin M in methanol-d_4

(5) HSQC Spectrum of xylogranatin M in methanol-d_4

(6) HMBC Spectrum of xylogranatin M in methanol-d_4

(7) A Segment of NOESY Spectrum of xylogranatin M in methanol-d_4

For xylogranatin N (9) (S118~S124)**:**

(1) IR spectrum of xylogranatin N

(2) HR-TOFMS of xylogranatin N

(3) ^{1}H NMR (500 MHz) Spectrum of xylogranatin N in methanol-d_4

(4) ^{13}C NMR (125 MHz) Spectrum and DEPT experiments of xylogranatin N in methanol-d_4

(5) HSQC Spectrum of xylogranatin N in methanol-d_4

(6) HMBC Spectrum of xylogranatin N in methanol-d_4

(7) A Segment of NOESY Spectrum of xylogranatin N in methanol-d_4

For xylogranatin O (10) (S125~S131)**:**

(1) IR spectrum of xylogranatin O

(2) HR-TOFMS of xylogranatin O

(3) ^{1}H NMR (500 MHz) Spectrum of xylogranatin O in methanol-d_4

(4) ^{13}C NMR (125 MHz) Spectrum and DEPT experiments of xylogranatin O in methanol-d_4

(5) HSQC Spectrum of xylogranatin O in methanol-d_4

(6) HMBC Spectrum of xylogranatin O in methanol-d_4

(7) A Segment of NOESY Spectrum of xylogranatin O in methanol-d_4

For xylogranatin P (11) (S132~S138)**:**

(1) IR spectrum of xylogranatin P

(2) HR-TOFMS of xylogranatin P

(3) ^{1}H NMR (500 MHz) Spectrum of xylogranatin P in methanol-d_4

(4) ^{13}C NMR (125 MHz) Spectrum and DEPT experiments of xylogranatin P in methanol-d_4

(5) HSQC Spectrum of xylogranatin P in methanol-d_4

(6) HMBC Spectrum of xylogranatin P in methanol-d_4

(7) A Segment of NOESY Spectrum of xylogranatin P in methanol-d_4

For xylogranatin Q (12) (S139~S151)**:**

(1) IR spectrum of xylogranatin Q

(2) HR-TOFMS of xylogranatin Q

(3) ^{1}H NMR (500 MHz) Spectrum of xylogranatin Q in methanol-d_4

(4) ^{13}C NMR (125 MHz) Spectrum of xylogranatin Q in methanol-d_4

(5) DEPT experiments of xylogranatin Q in methanol-d_4

(6) ^{1}H-^{1}H COSY Spectrum of xylogranatin Q in methanol-d_4

(7) HSQC Spectrum of xylogranatin Q in methanol-d_4

(8) HMBC Spectrum of xylogranatin Q in methanol-d_4

(9) A Segment of HMBC Spectrum of xylogranatin Q in methanol-d_4

(10) A Segment of NOESY Spectrum of xylogranatin Q in methanol-d_4

(11) A Segment of NOESY Spectrum of xylogranatin Q in methanol-d_4

(12) A Segment of NOESY Spectrum of xylogranatin Q in methanol-d_4

(13) A Segment of NOESY Spectrum of xylogranatin Q in methanol-d_4

For xylogranatin R (13) (S152~S165)**:**

(1) IR spectrum of xylogranatin R

(2) HR-TOFMS of xylogranatin R

(3) ^{1}H NMR (500 MHz) Spectrum of xylogranatin R in $CDCl_3$

(4) ^{13}C NMR (125 MHz) Spectrum and DEPT experiments of xylogranatin R in $CDCl_3$

(5) ^{1}H-^{1}H COSY Spectrum of xylogranatin R in $CDCl_3$

(6) A Segment of ^{1}H-^{1}H COSY Spectrum of xylogranatin R in $CDCl_3$

(7) HSQC Spectrum of xylogranatin R in $CDCl_3$

(8) HMBC Spectrum of xylogranatin R in $CDCl_3$

(9) A Segment of HMBC Spectrum of xylogranatin R in $CDCl_3$

(10) A Segment of HMBC Spectrum of xylogranatin R in $CDCl_3$

(11) A Segment of HMBC Spectrum of xylogranatin R in $CDCl_3$

(12) A Segment of HMBC Spectrum of xylogranatin R in $CDCl_3$

(13) A Segment of HMBC Spectrum of xylogranatin R in $CDCl_3$

(14) NOESY Spectrum of xylogranatin R in $CDCl_3$

For xylogranatins C and D (S166~S171)**:**

(1) HR-TOFMS of xylogranatin C

(2) ^{1}H NMR (500 MHz) Spectrum of xylogranatin C in $CDCl_3$

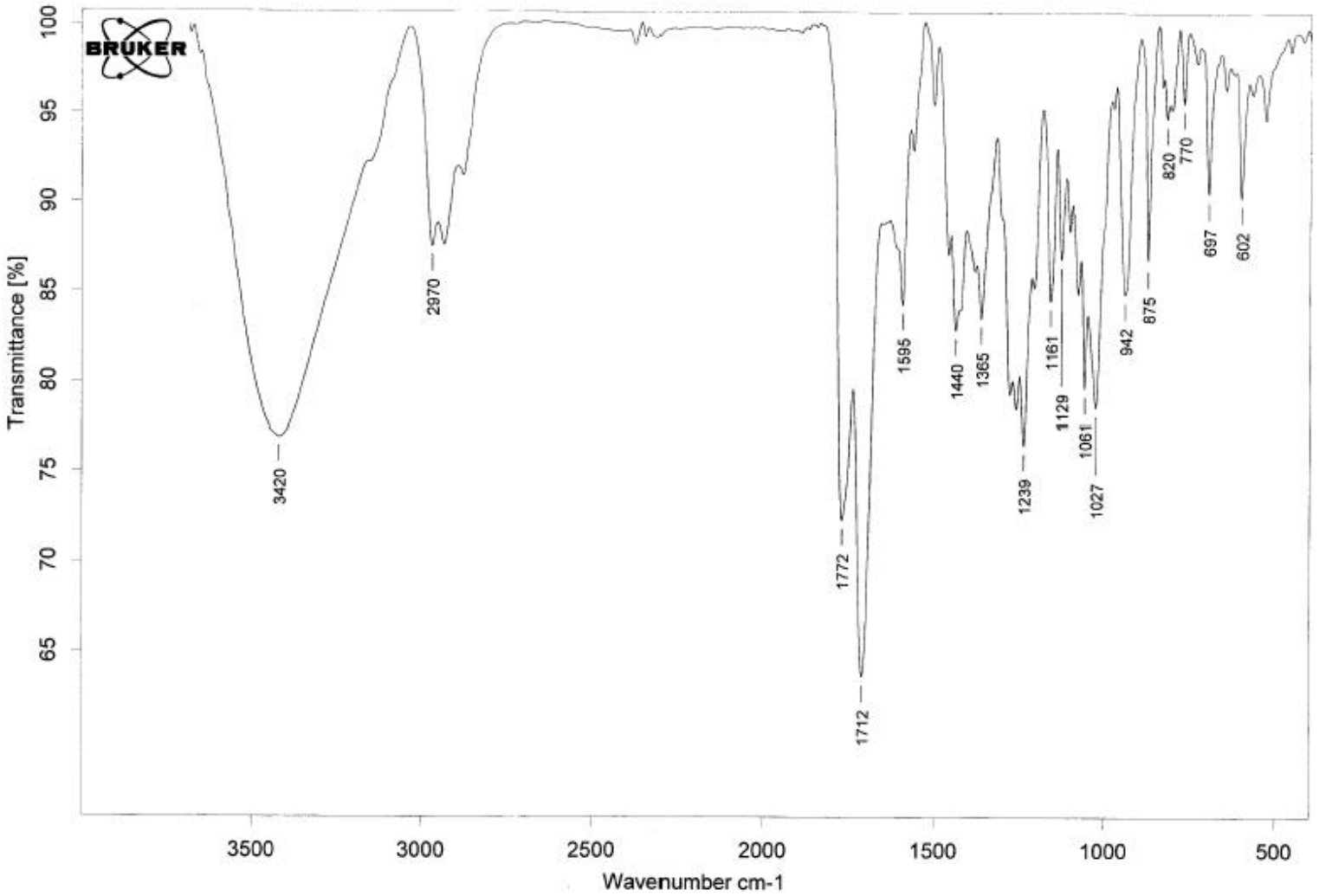
(3) ^{13}C NMR (125 MHz) Spectrum and DEPT experiments of xylogranatin C in $CDCl_3$

(4) HR-TOFMS of xylogranatin D

(5) ^{1}H NMR (500 MHz) Spectrum of xylogranatin D in $CDCl_3$

(6) ^{13}C NMR (125 MHz) Spectrum and DEPT experiments of xylogranatin D in $CDCl_3$

IR spectrum of xylogranatin F (**1**)



HR-TOFMS of xylogranatin F (**1**)

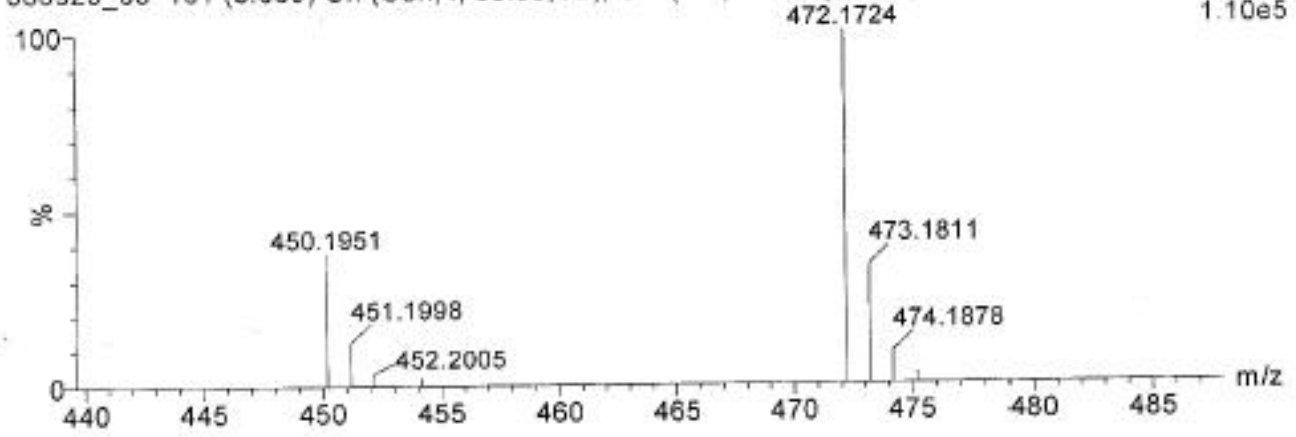
Elemental Composition Report

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

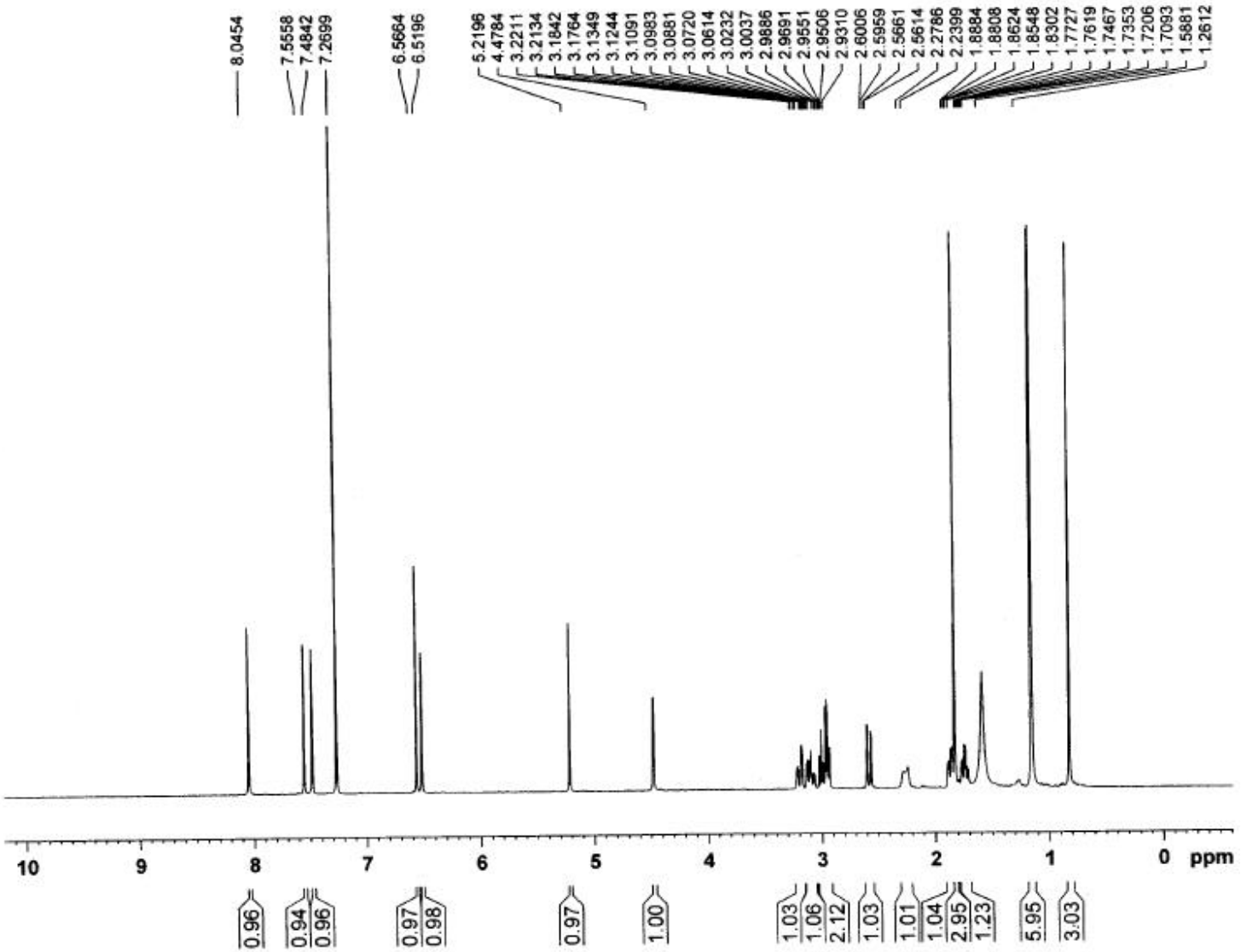
Monoisotopic Mass, Odd and Even Electron Ions
48 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

Minimum:				-1.5		
Maximum:		200.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
472.1724	472.1736	-1.2	-2.6	13.5	2	C26 H27 N O6 23Na
	472.1760	-3.6	-7.7	16.5	1	C28 H26 N O6

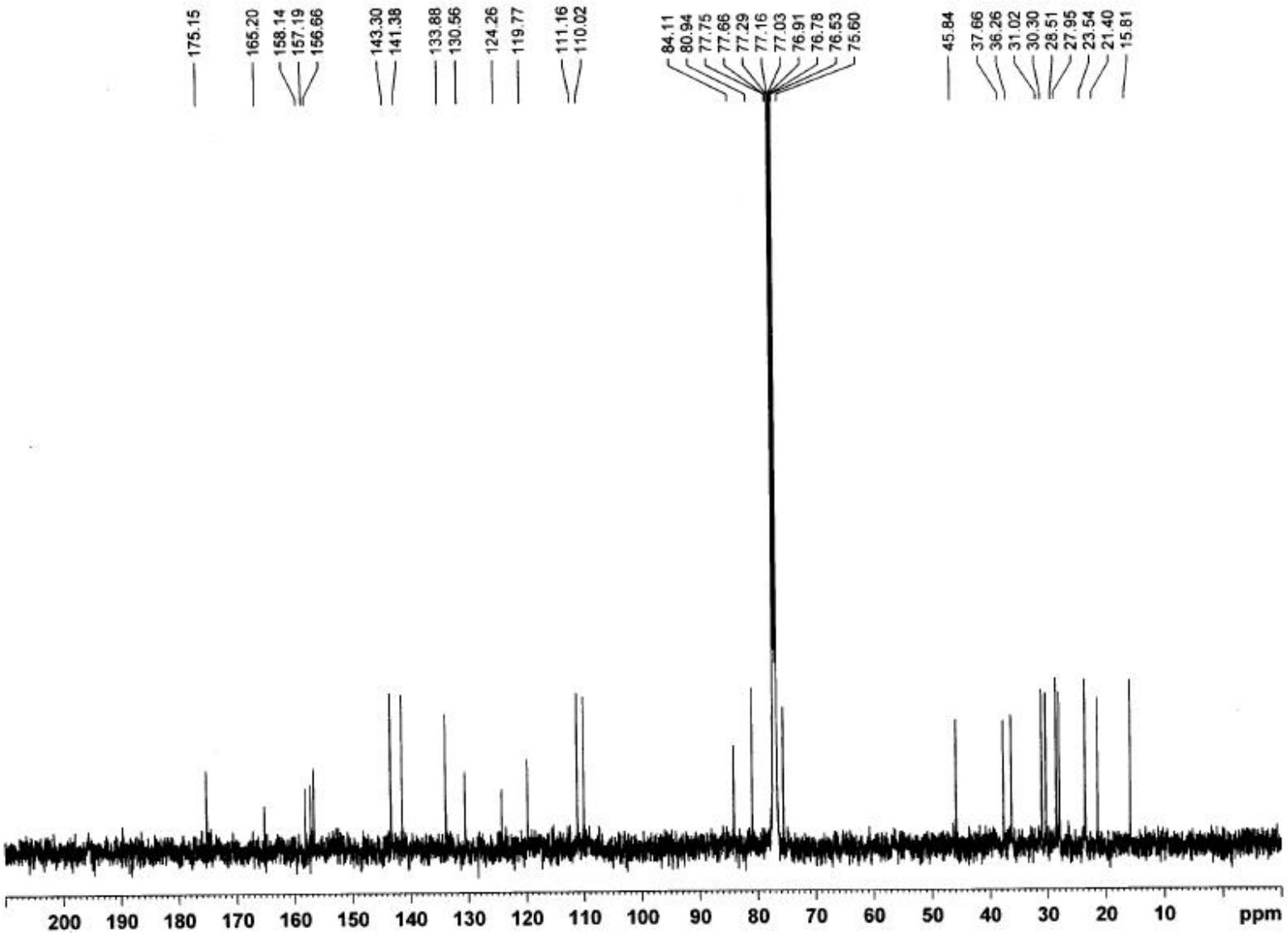
Wu07
060929_06 161 (3.069) Cn (Cen,4, 80.00, Ar); Sm (SG, 2x3.00); Cm (149:167) TOF MS ES+
1.10e5



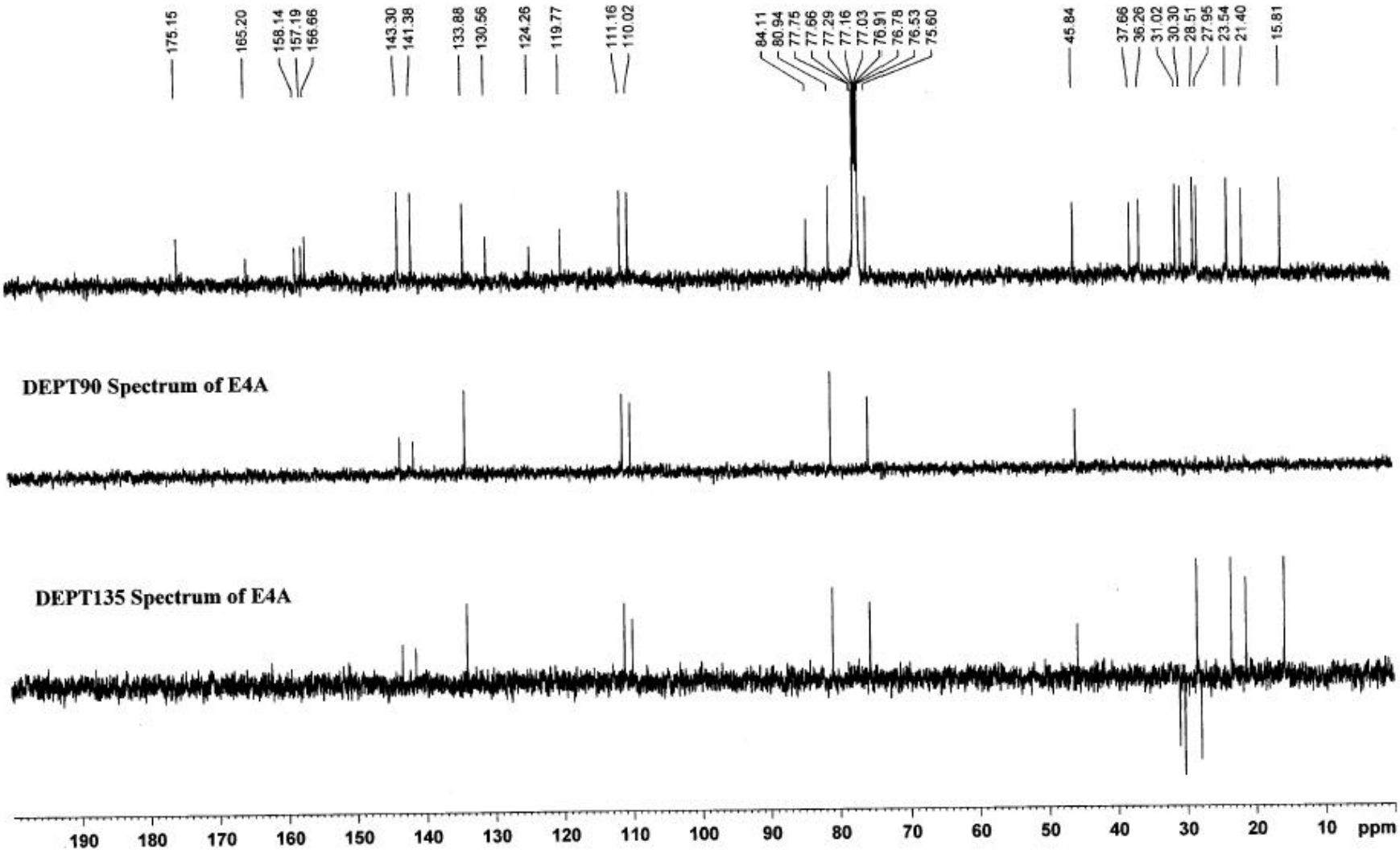
^{1}H NMR (500 MHz) Spectrum of xylogranatin F (**1**) in $CDCl_3$



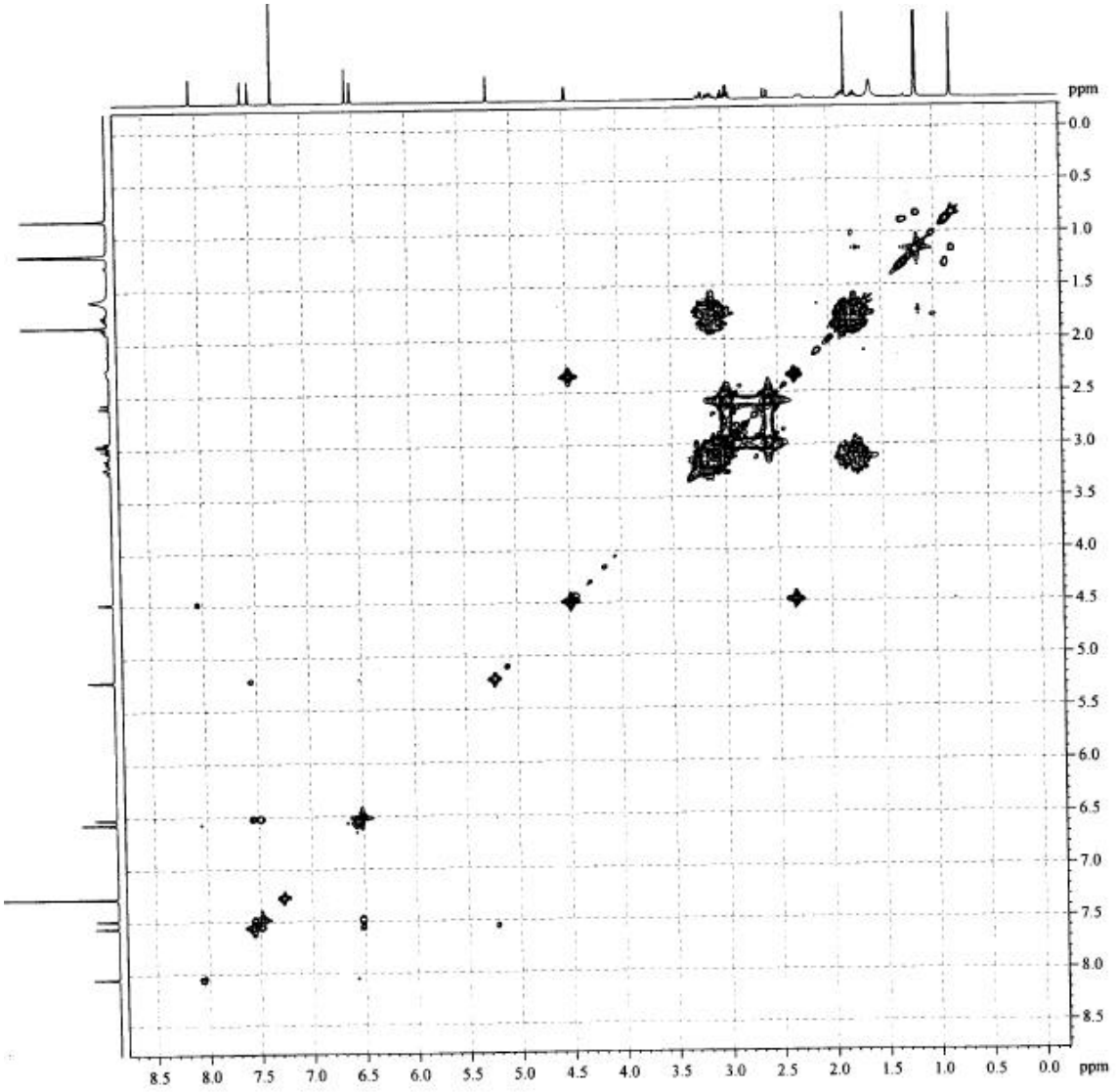
^{13}C NMR (125 MHz) Spectrum of xylogranatin F (**1**) in $CDCl_3$



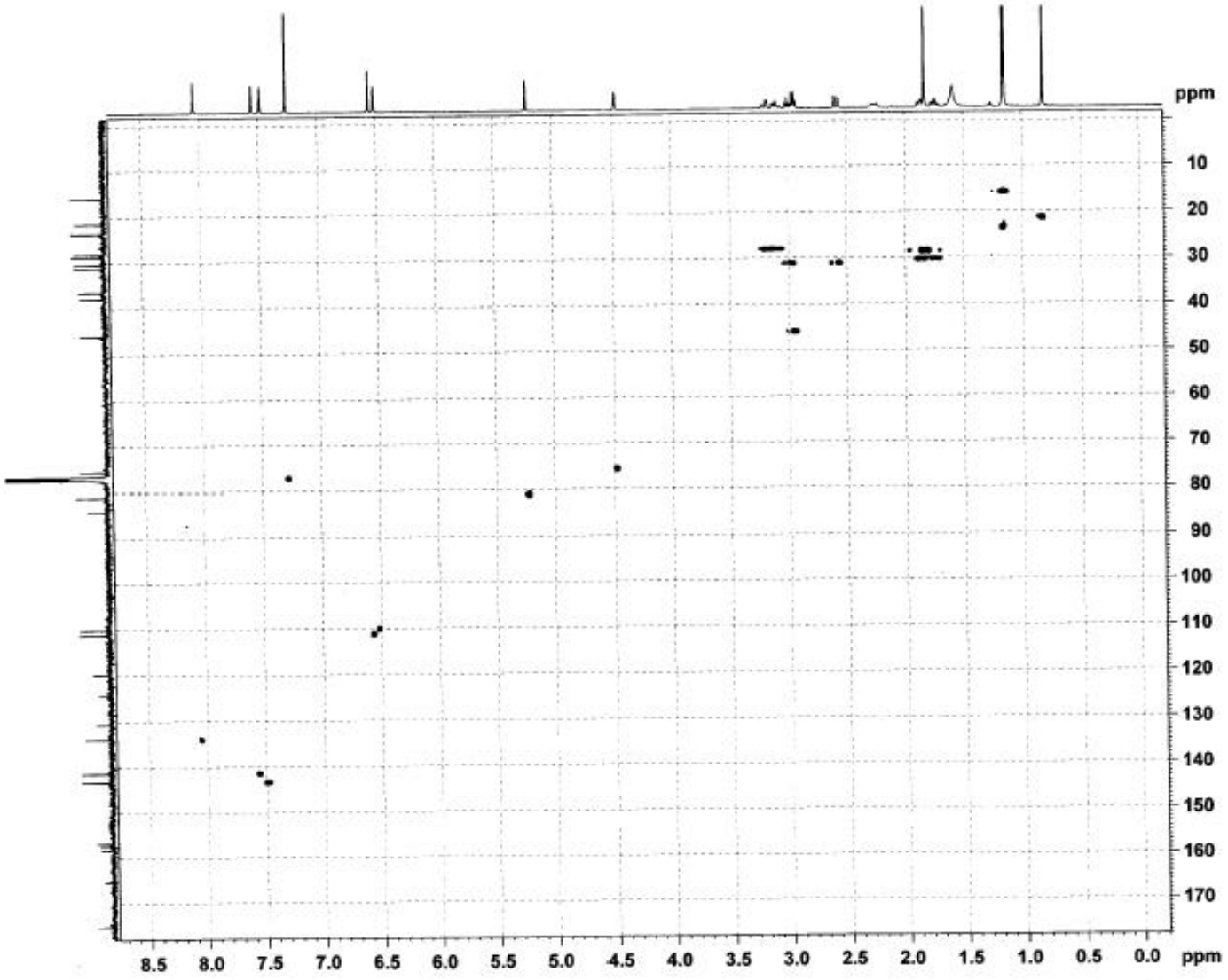
DEPT 90° and 135° experiments of xylogranatin F (**1**) in $CDCl_3$



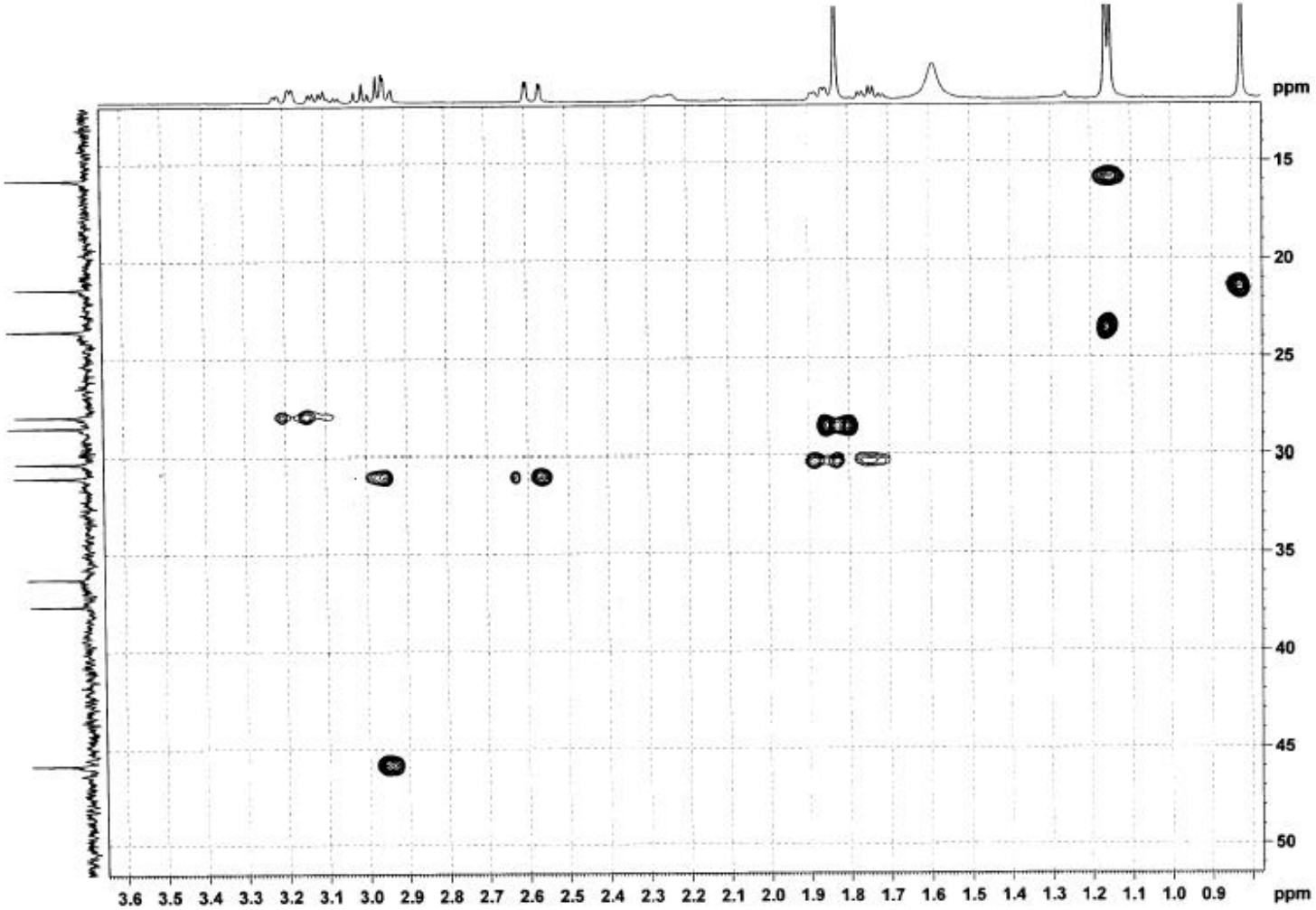
^{1}H-^{1}H COSY Spectrum of xylogranatin F (**1**) in $CDCl_3$



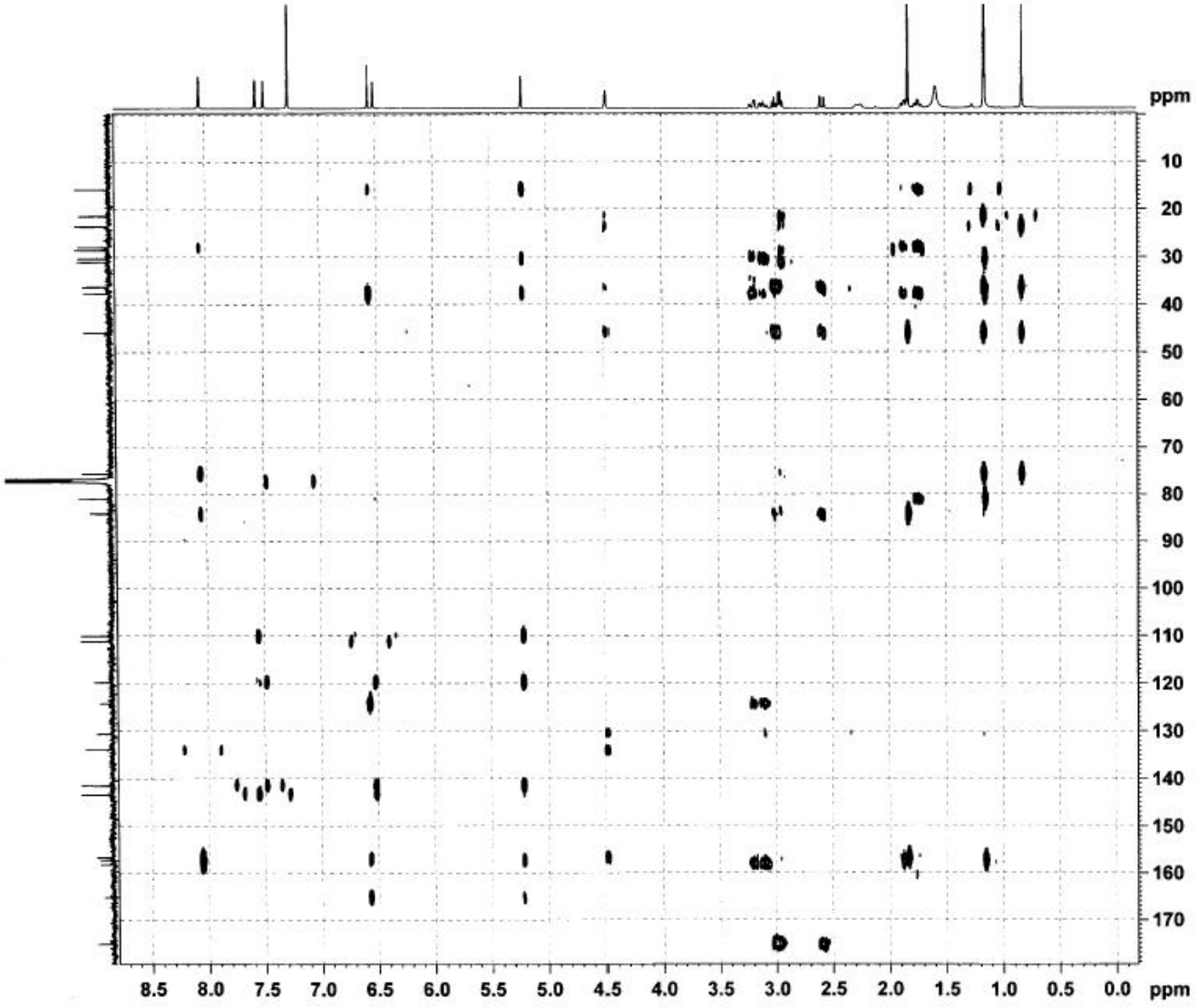
HSQC Spectrum of xylogranatin F (**1**) in $CDCl_3$



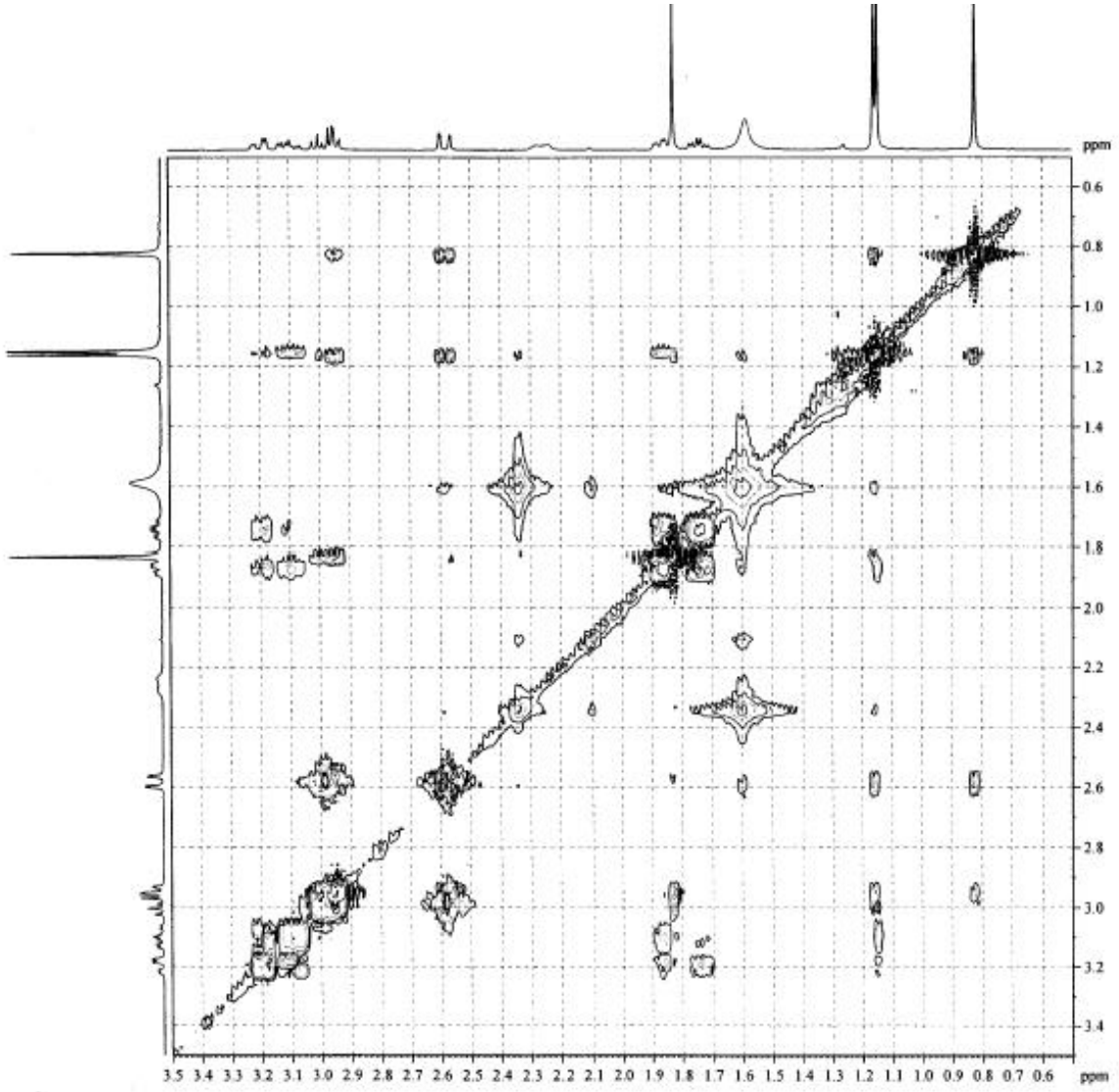
A segment of HSQC Spectrum of xylogranatin F (**1**) in $CDCl_3$



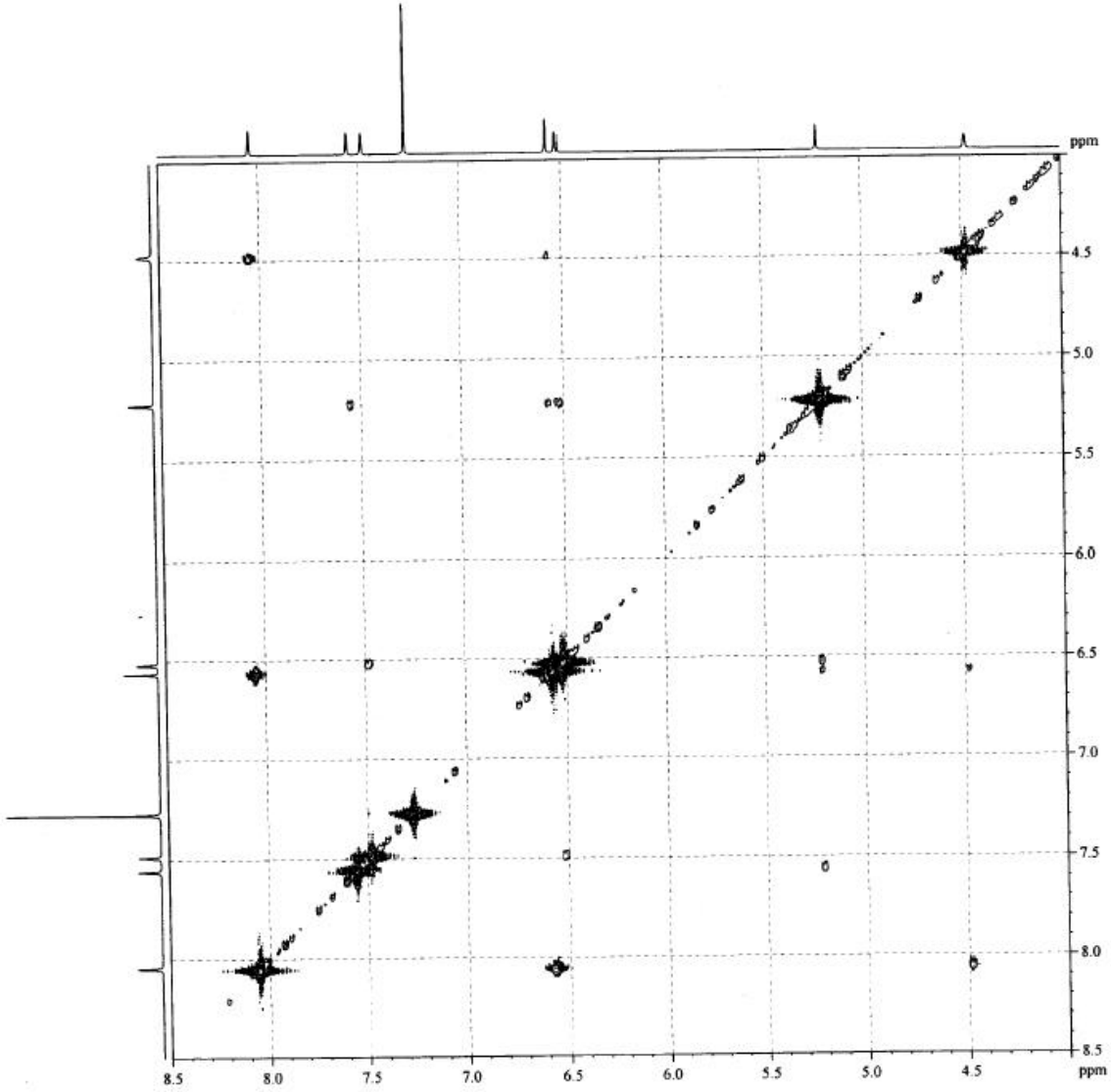
HMBC Spectrum of xylogranatin F (**1**) in $CDCl_3$



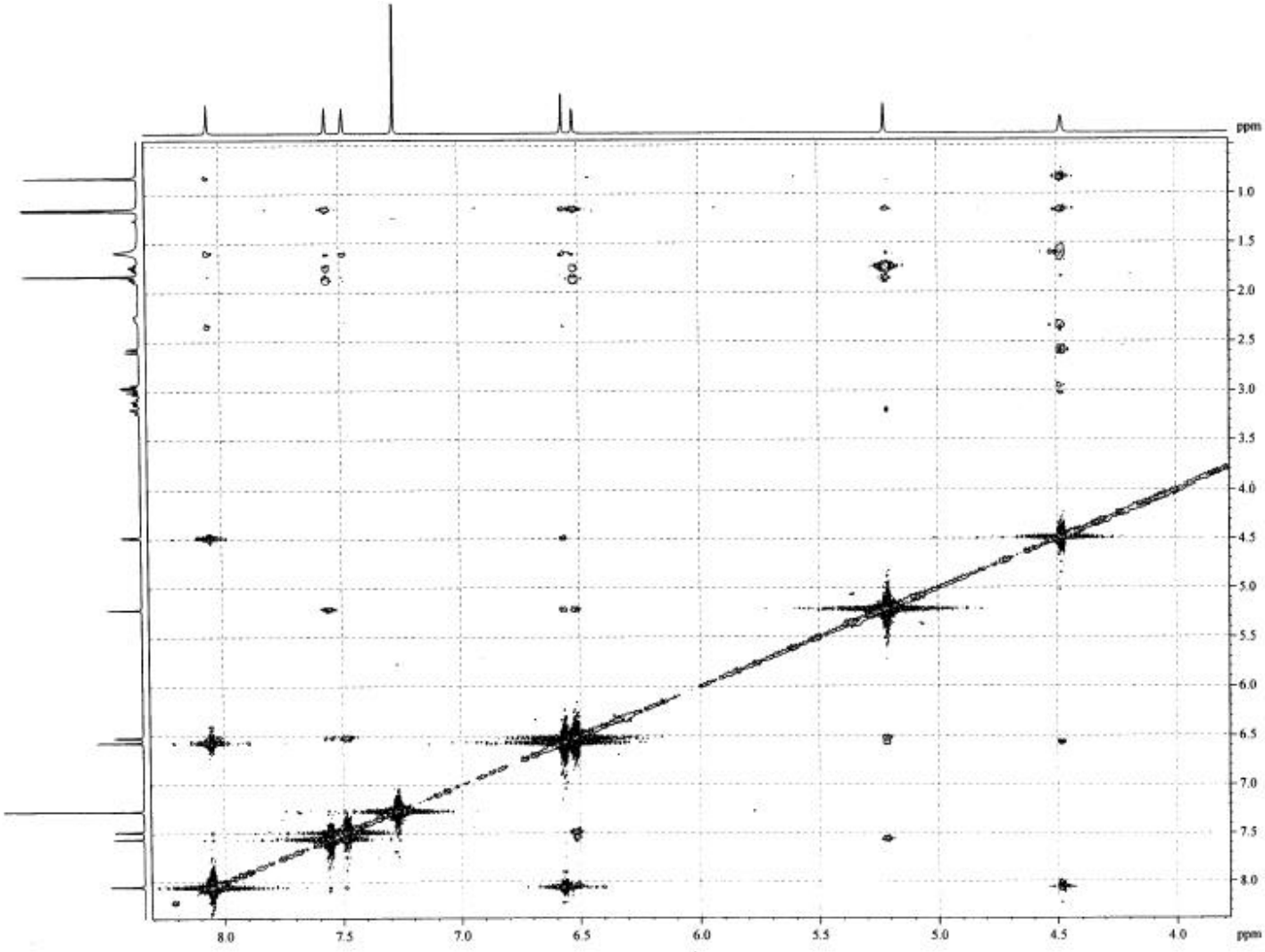
A segment of NOESY Spectrum of xylogranatin F (**1**) in $CDCl_3$



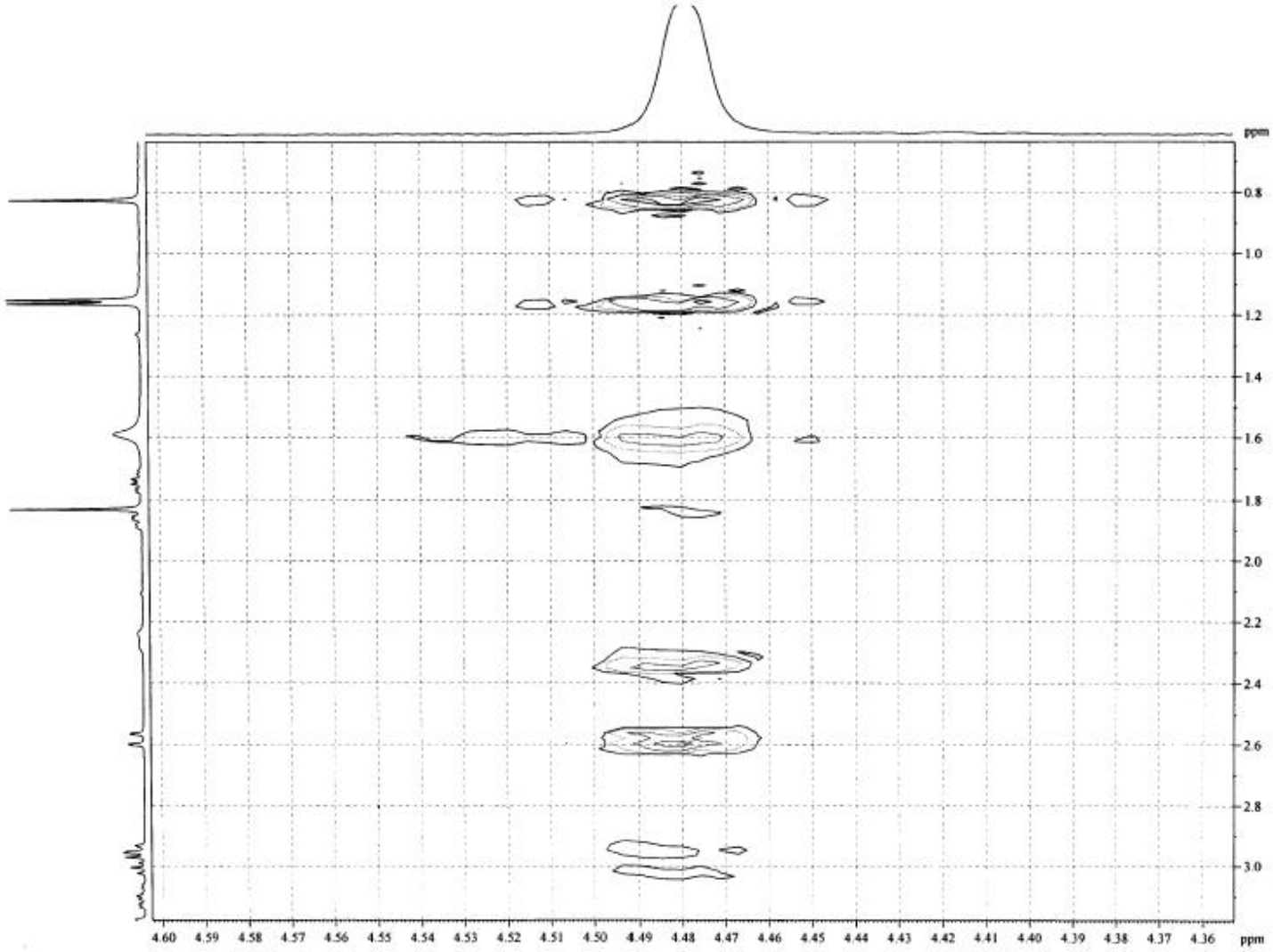
A segment of NOESY Spectrum of xylogranatin F (**1**) in $CDCl_3$



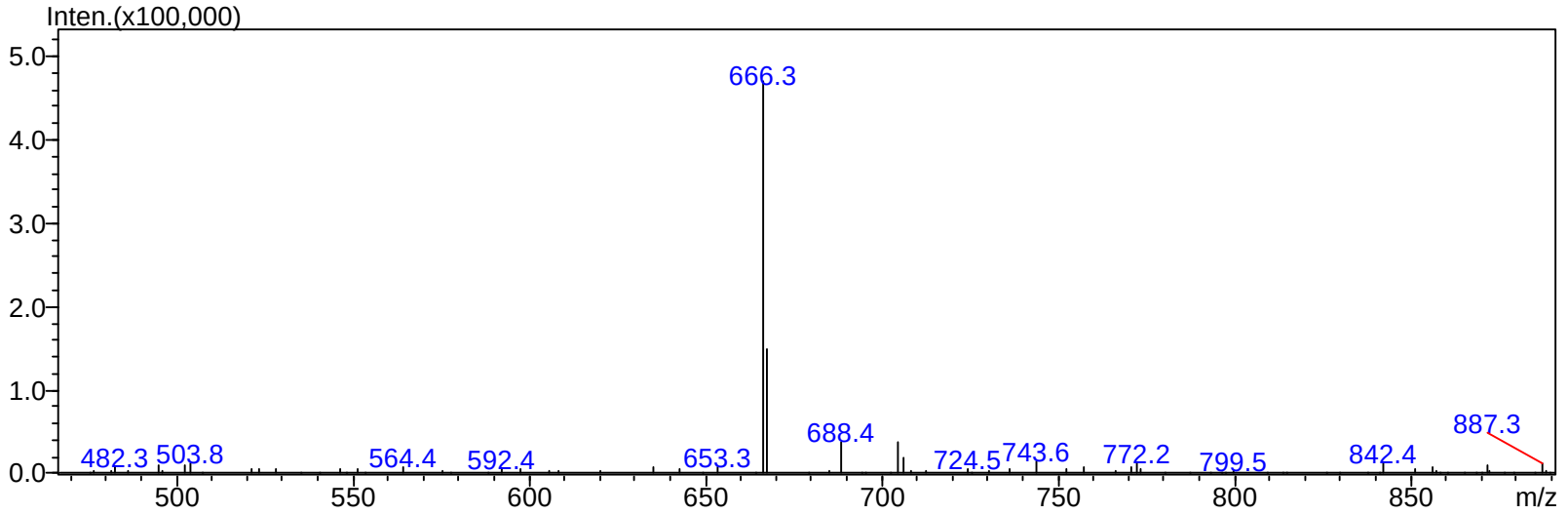
A segment of NOESY Spectrum of xylogranatin F (**1**) in $CDCl_3$



A segment of NOESY Spectrum of xylogranatin F (**1**) in $CDCl_3$



ESI-MS of **1s**


Inten.(x100,000)
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4.0
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2.0
1.0
0.0
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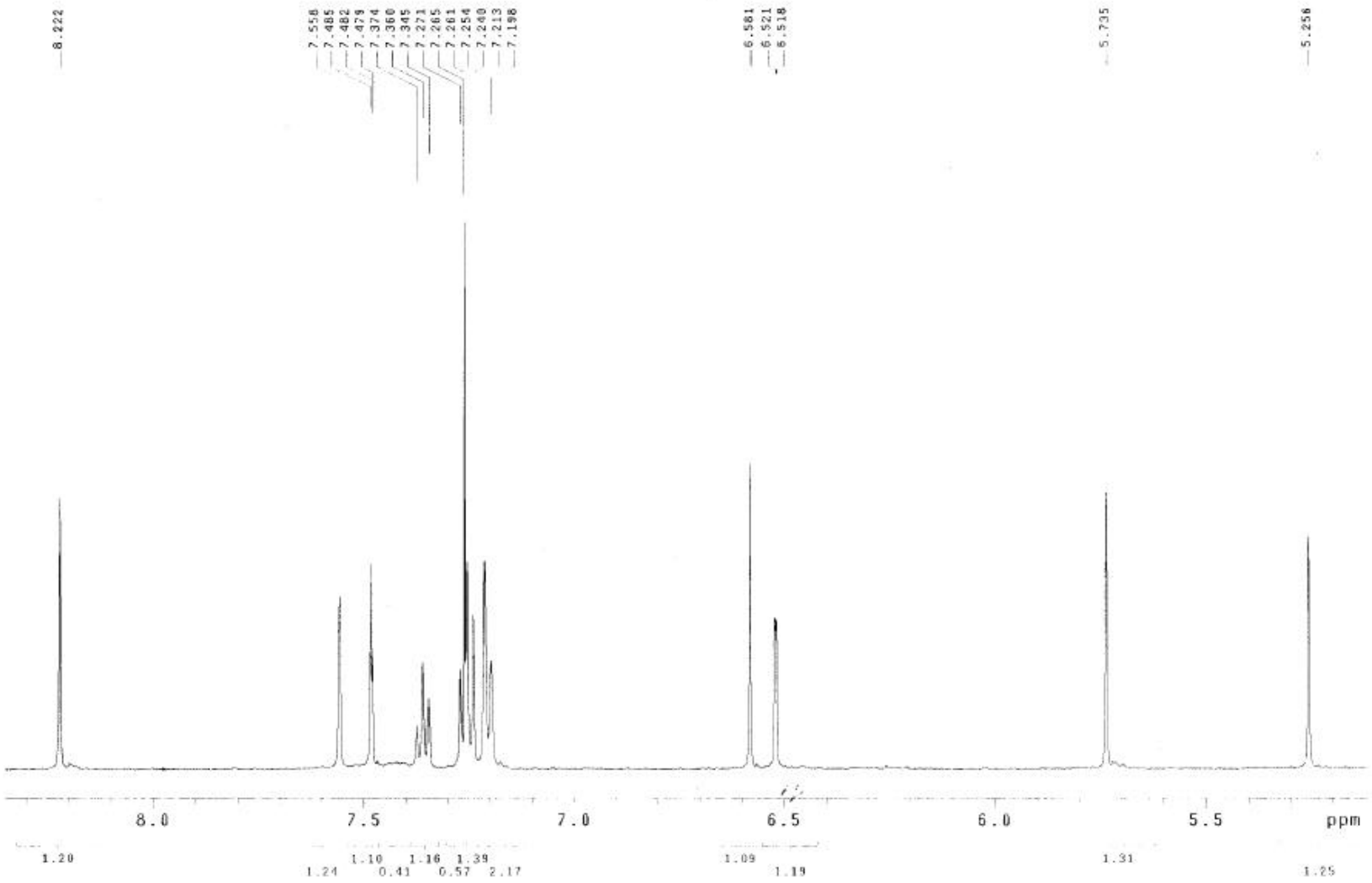
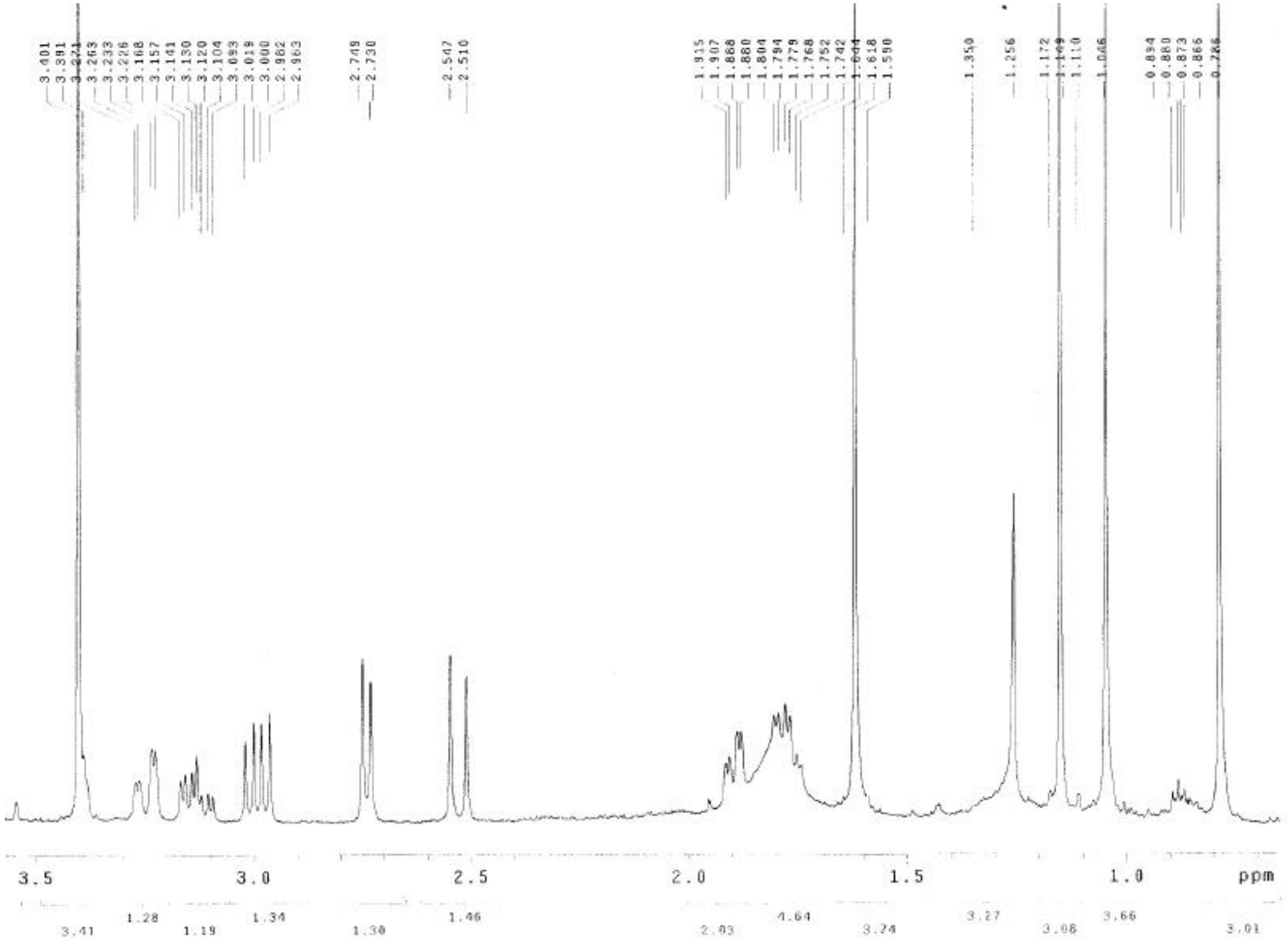
482.3
503.8
564.4
592.4
653.3
688.4
724.5
743.6
772.2
799.5
842.4
887.3
500
550
600
650
700
750
800
850
m/z

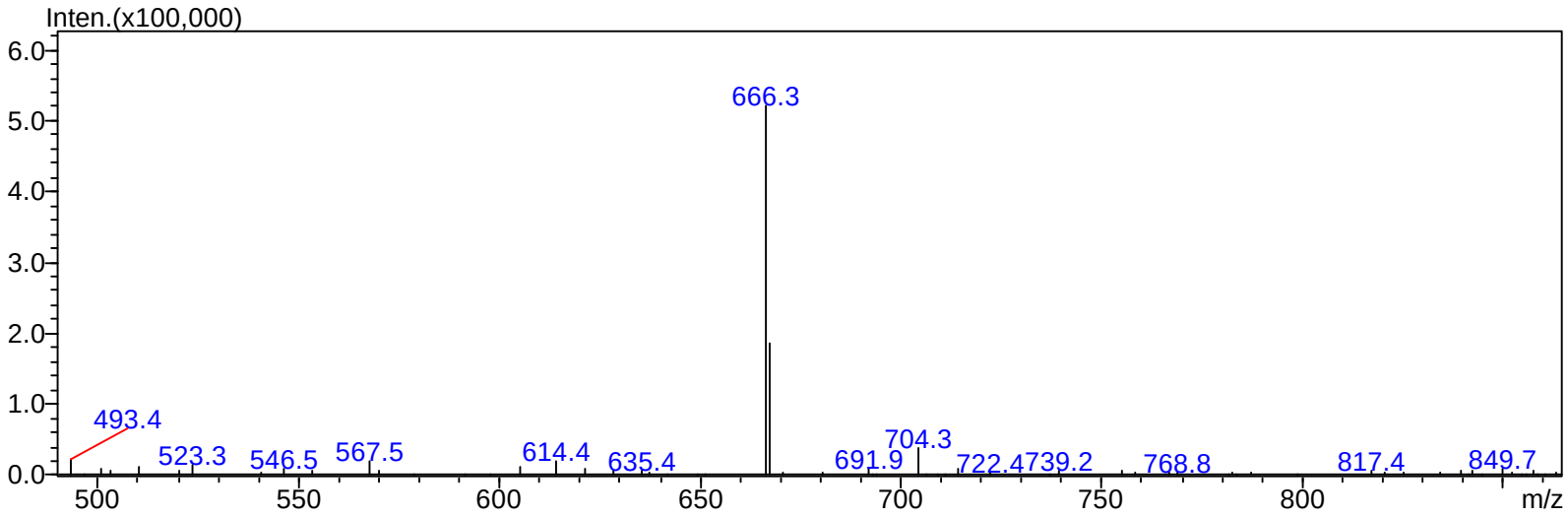
A Segment of ^{1}H NMR (500 MHz) of **1s** in $CDCl_3$



A Segment of ^{1}H NMR (500 MHz) of **1s** in $CDCl_3$



ESI-MS of **1r**


Inten.(x100,000)
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3.0
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1.0
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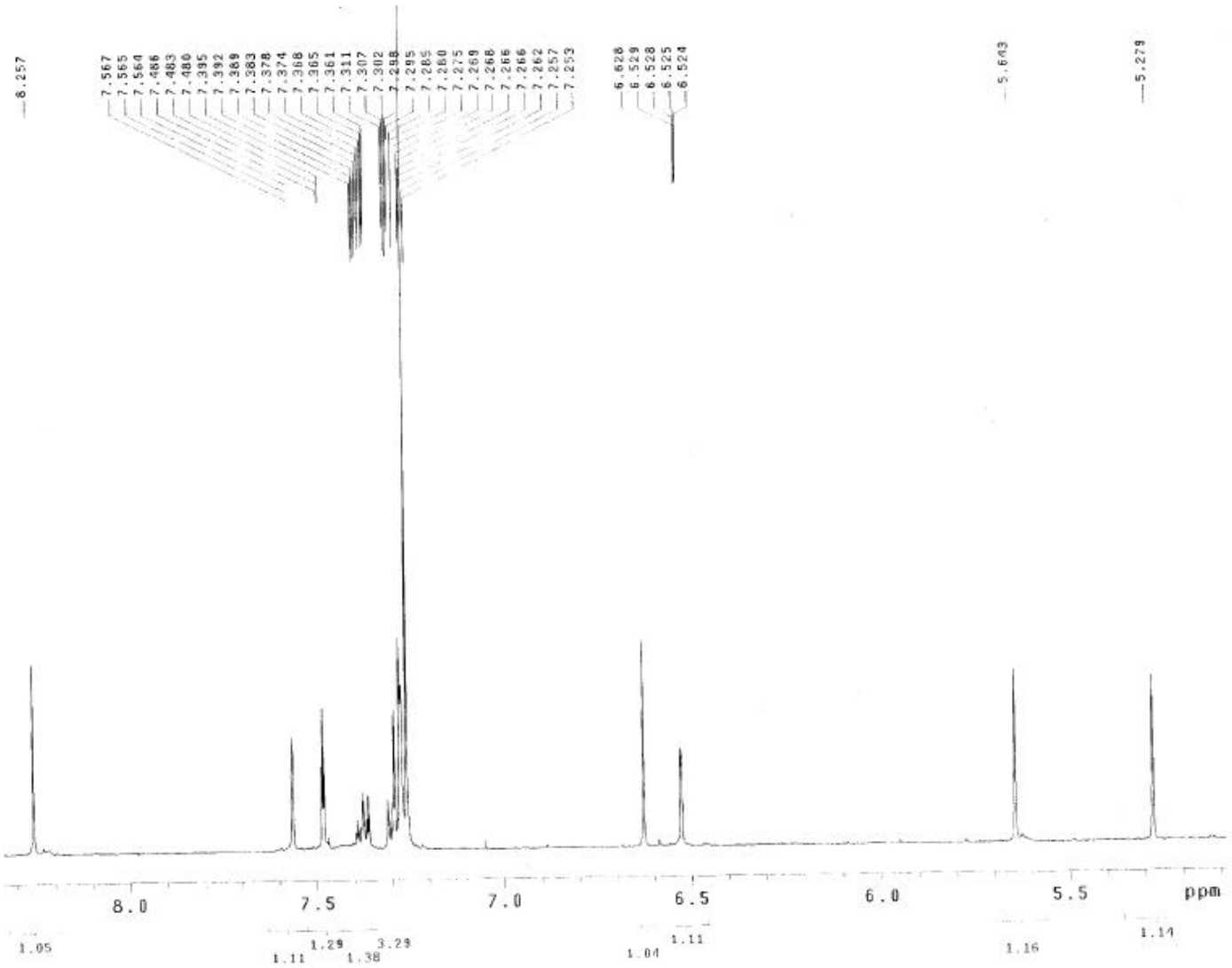
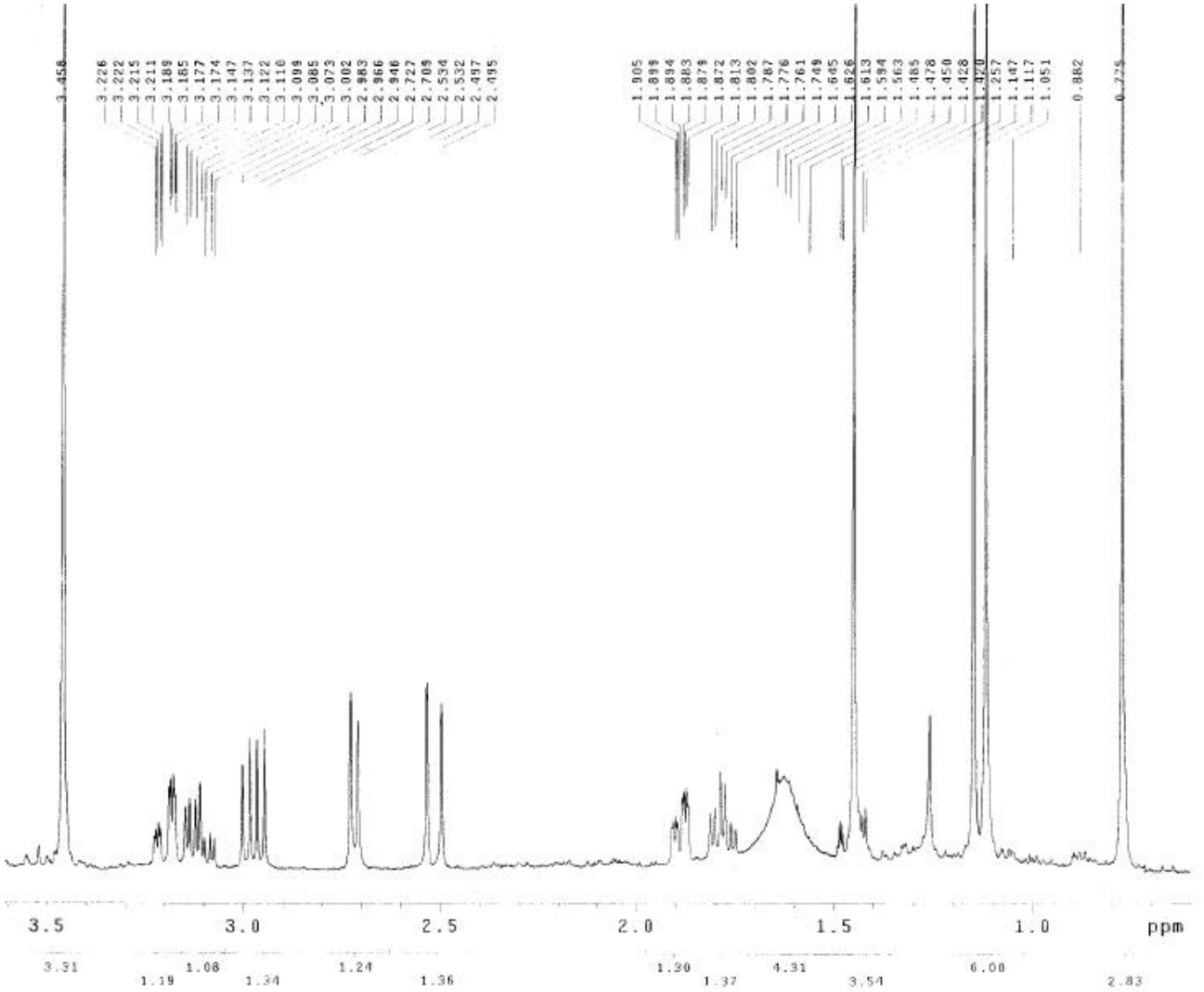
523.3
546.5
567.5
614.4
635.4
691.9
704.3
722.4
739.2
768.8
817.4
849.7
500
550
600
650
700
750
800
m/z

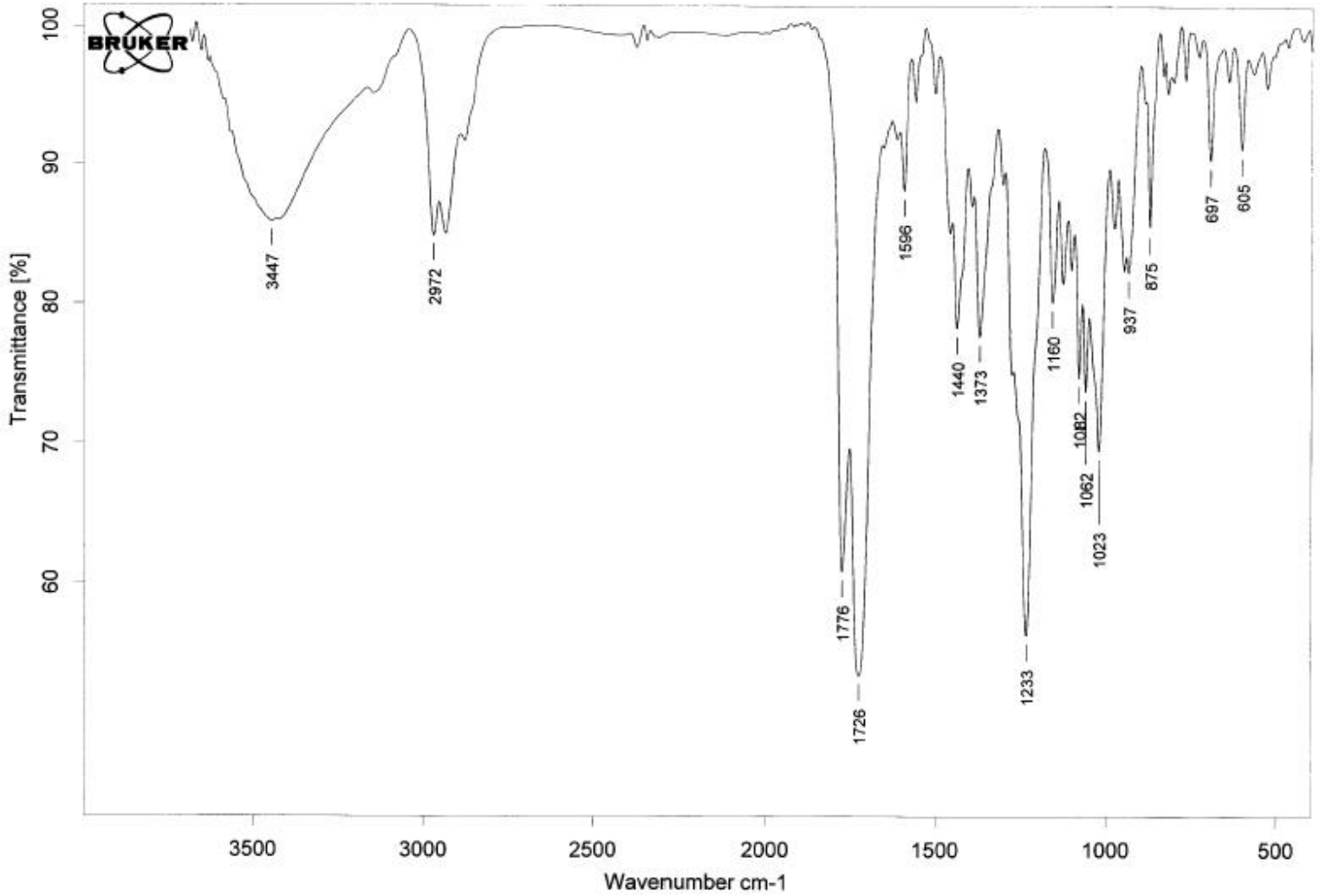
A Segment of ^{1}H NMR (500 MHz) of **1r** in $CDCl_3$



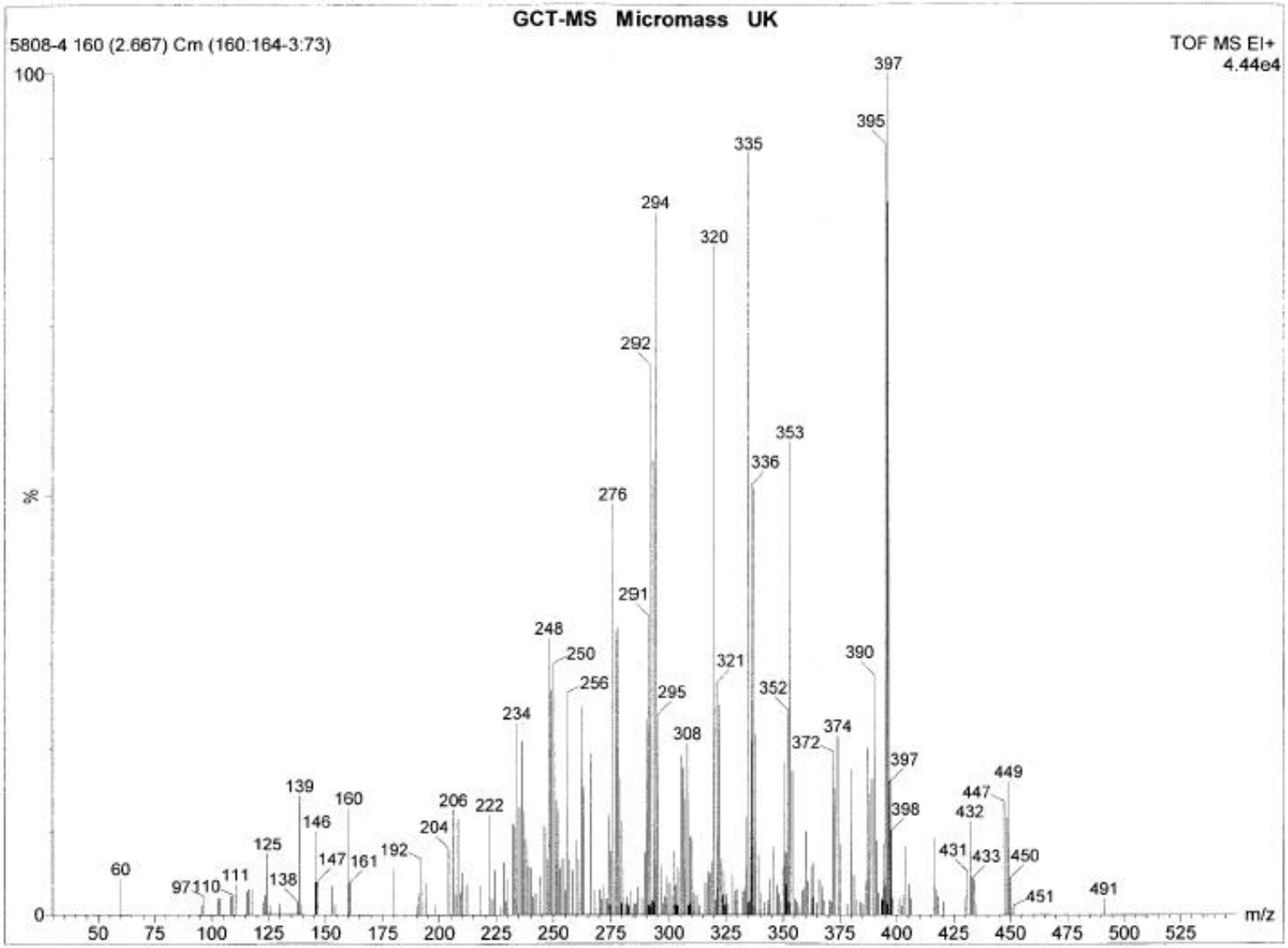
A Segment of ^{1}H NMR (500 MHz) of **1r** in $CDCl_3$



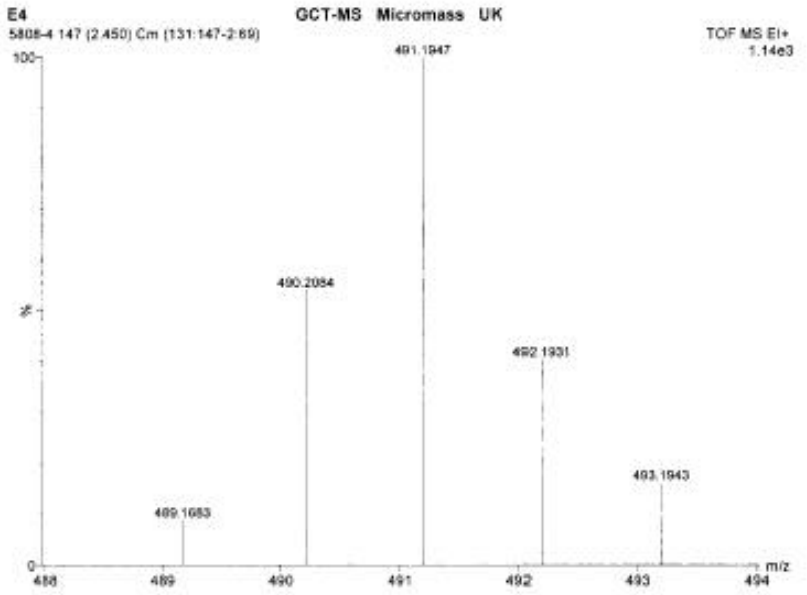
IR spectrum of xylogranatin G (**2**)



TOFMS of xylogranatin G (**2**)



HR-TOFMS of xylogranatin G (**2**)



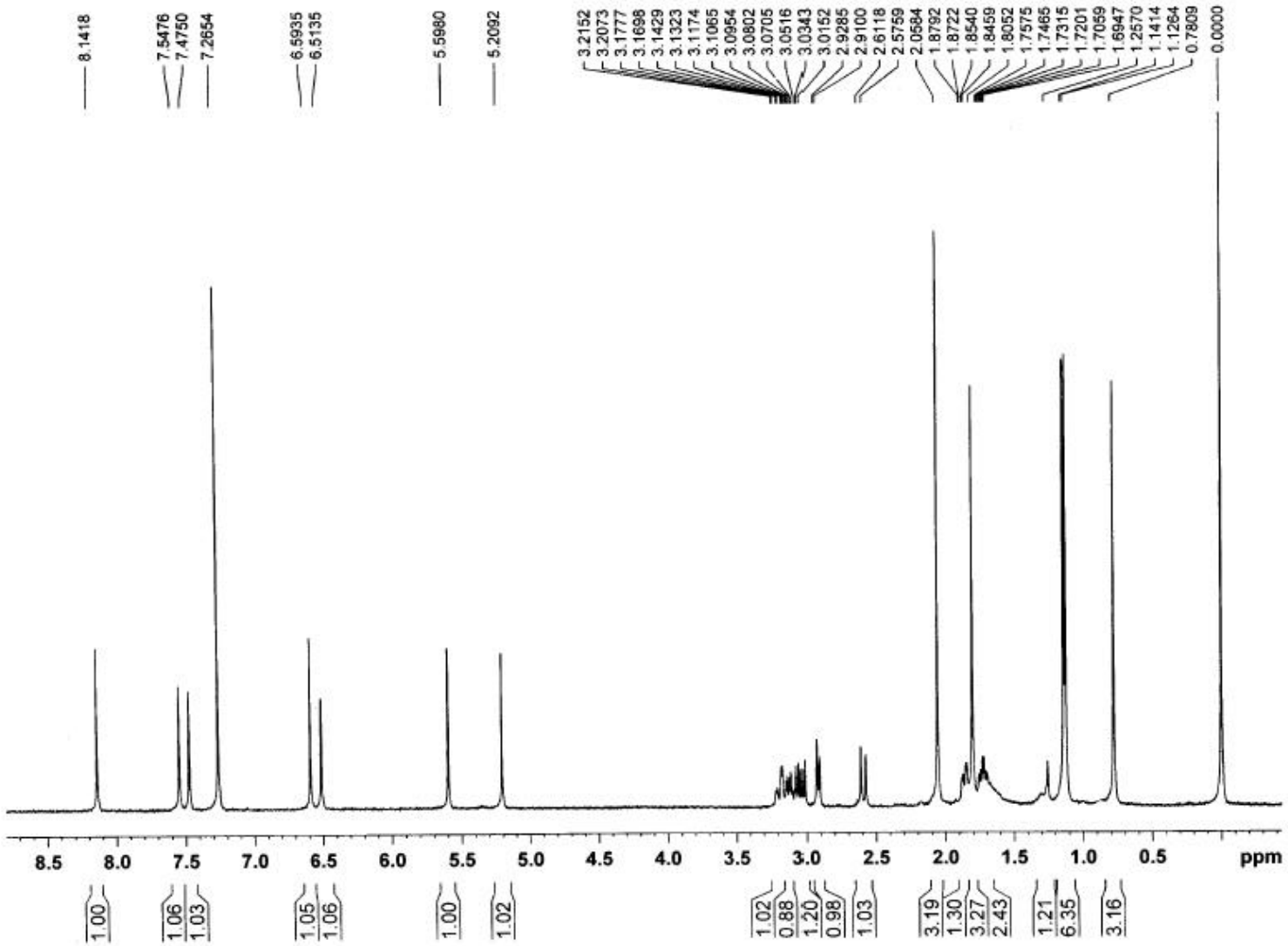
Elemental Composition Report

Tolerance = 2.0 mDa / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

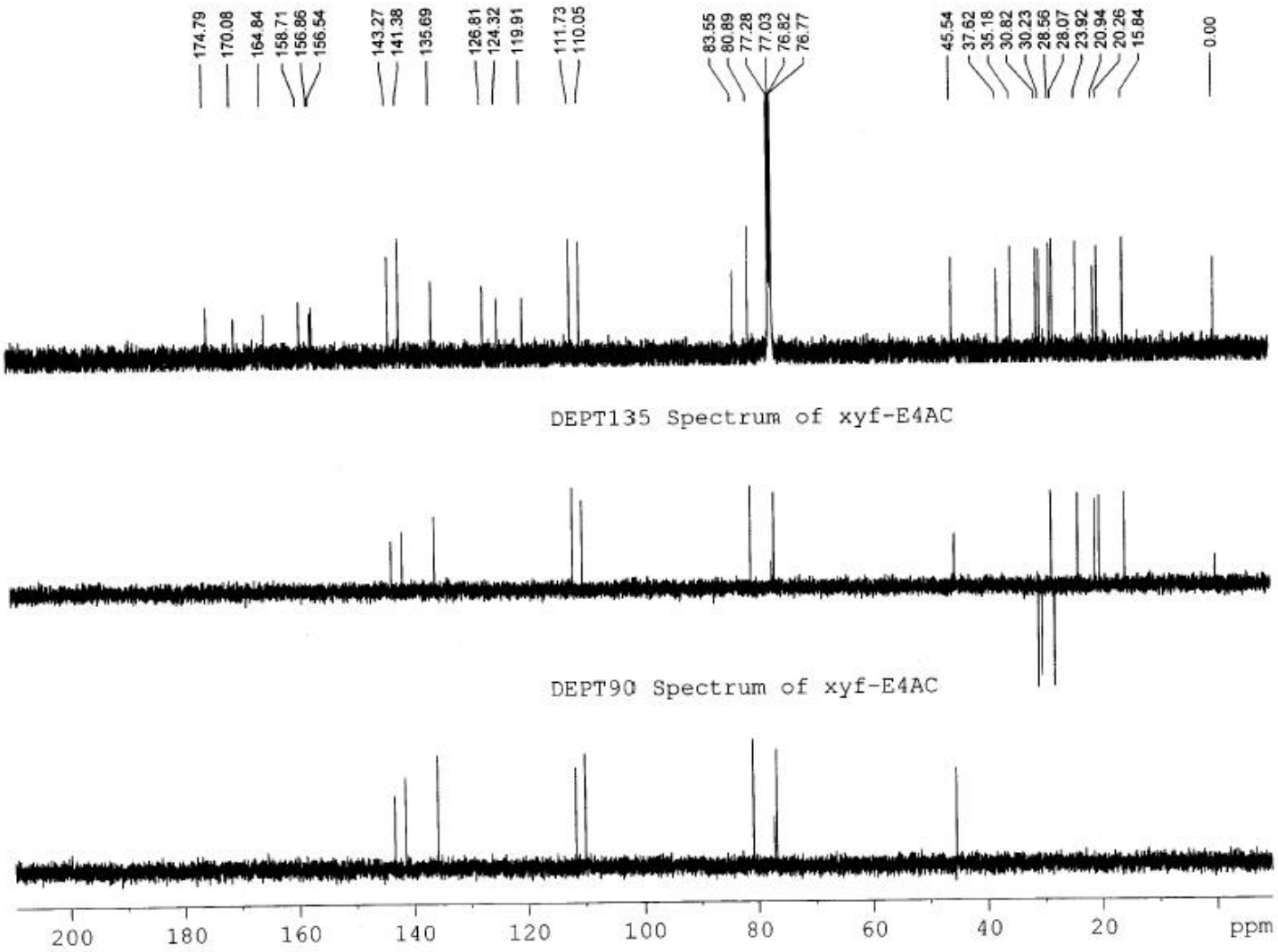
Monoisotopic Mass, Odd and Even Electron Ions
190 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Minimum:	80.00				-1.5		
Maximum:	100.00		2.0	5.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
491.1947	100.00	491.1944	0.3	0.6	15.0	1	C28 H29 N O7

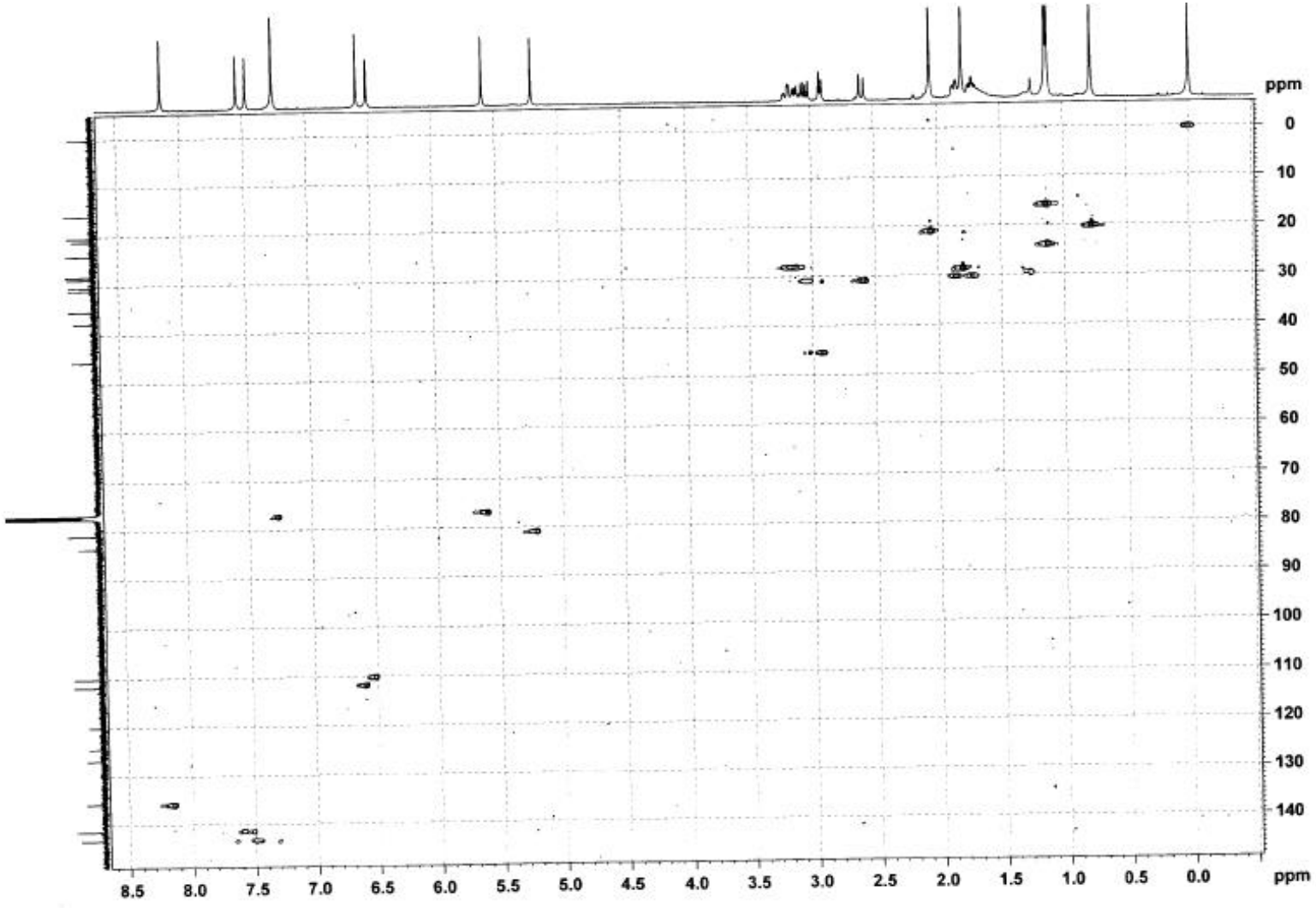
^{1}H NMR (500 MHz) Spectrum of xylogranatin G (**2**) in $CDCl_3$



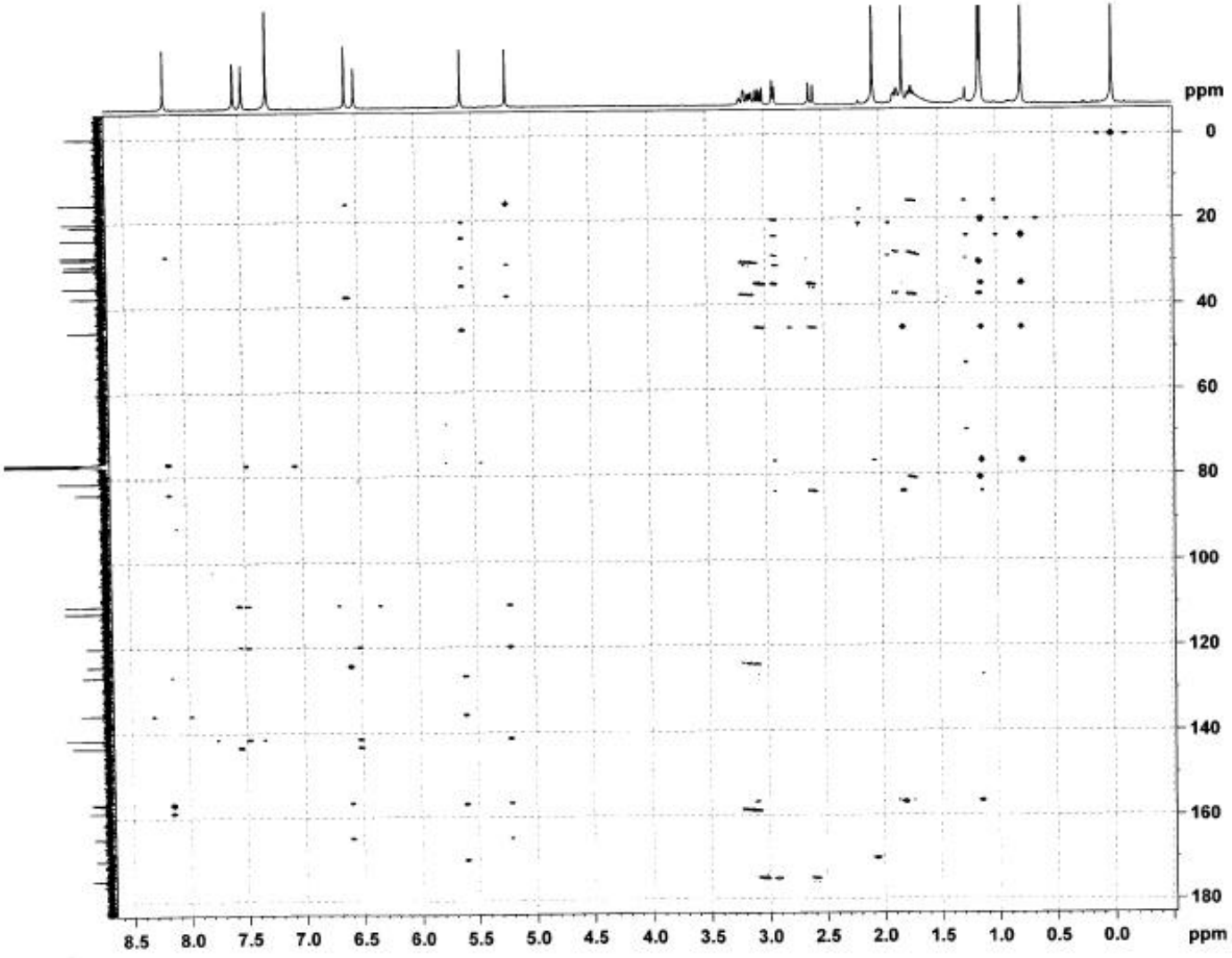
^{13}C NMR (125 MHz) Spectrum and DEPT experiments of xylogranatin G (**2**) in $CDCl_3$



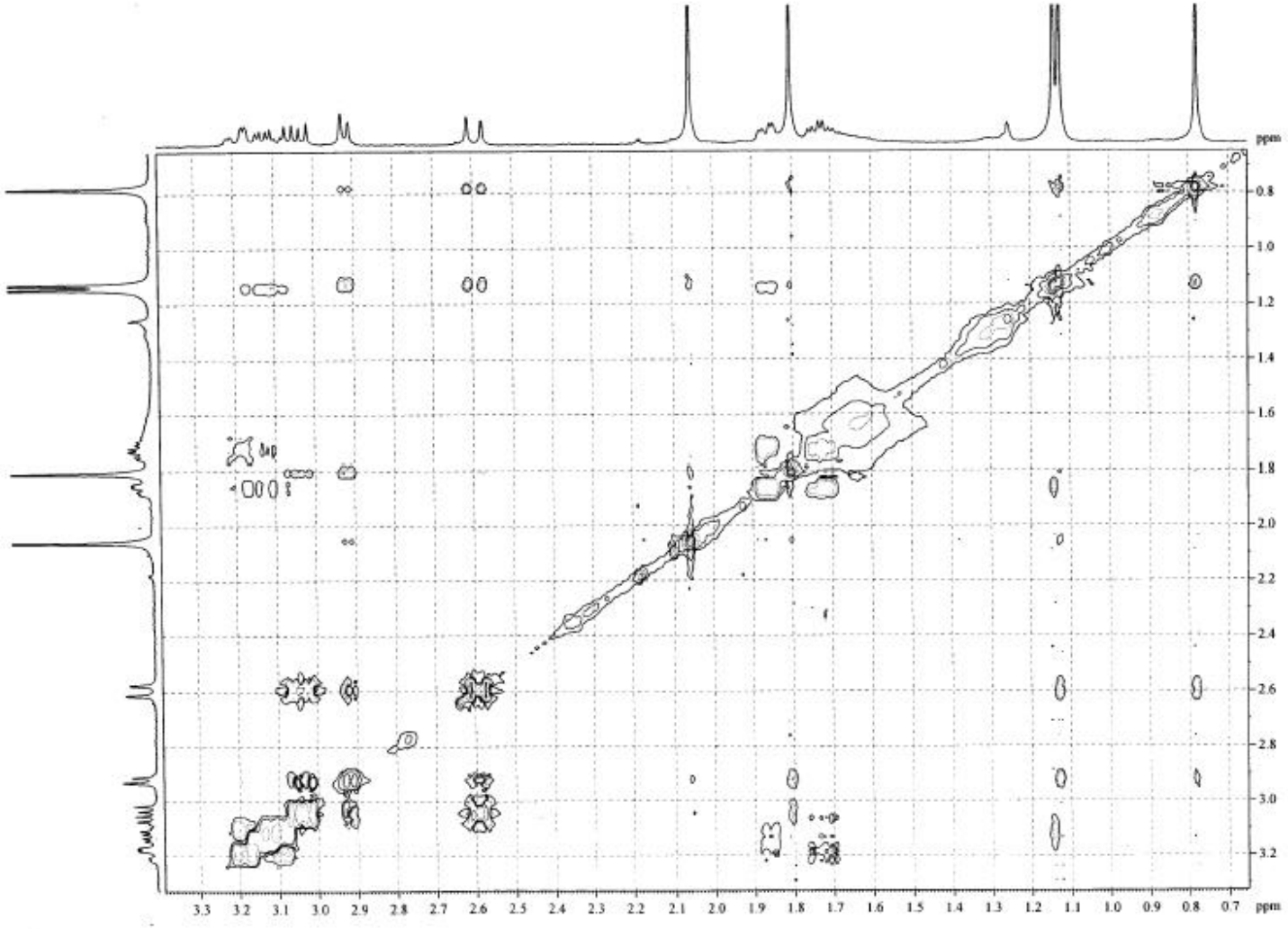
HSQC Spectrum of xylogranatin G (**2**) in $CDCl_3$



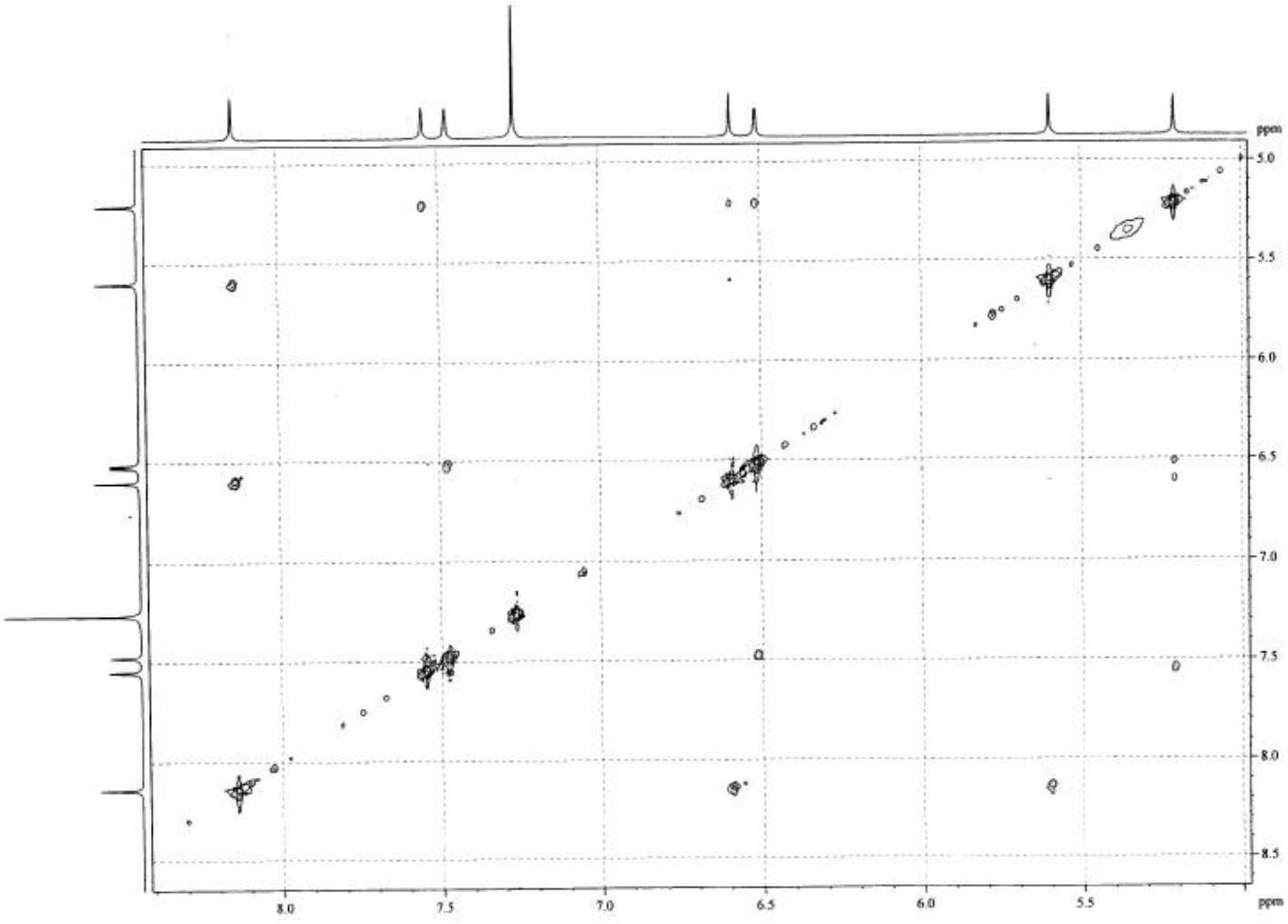
HMBC Spectrum of xylogranatin G (**2**) in $CDCl_3$



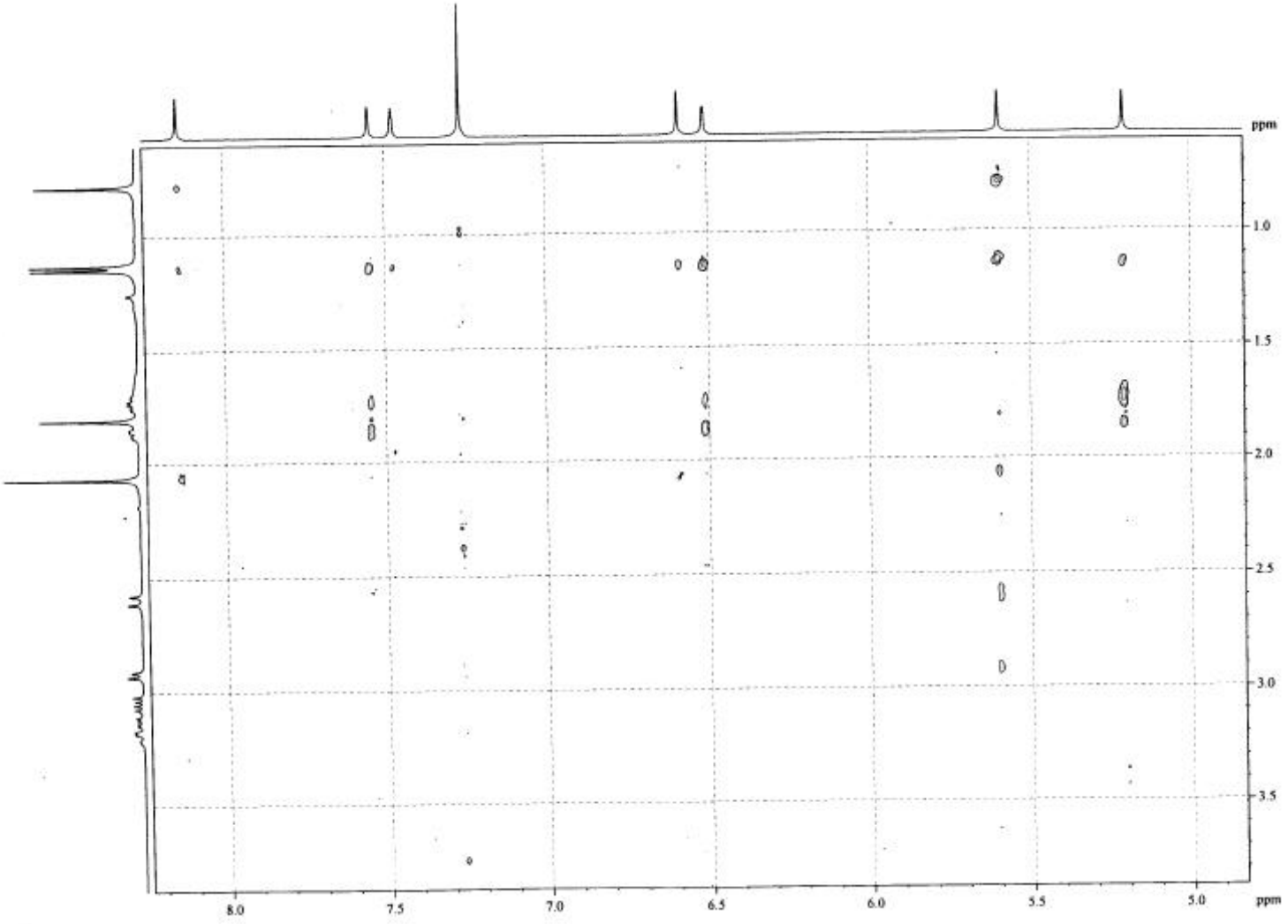
A Segment of NOESY Spectrum of xylogranatin G (**2**) in $CDCl_3$



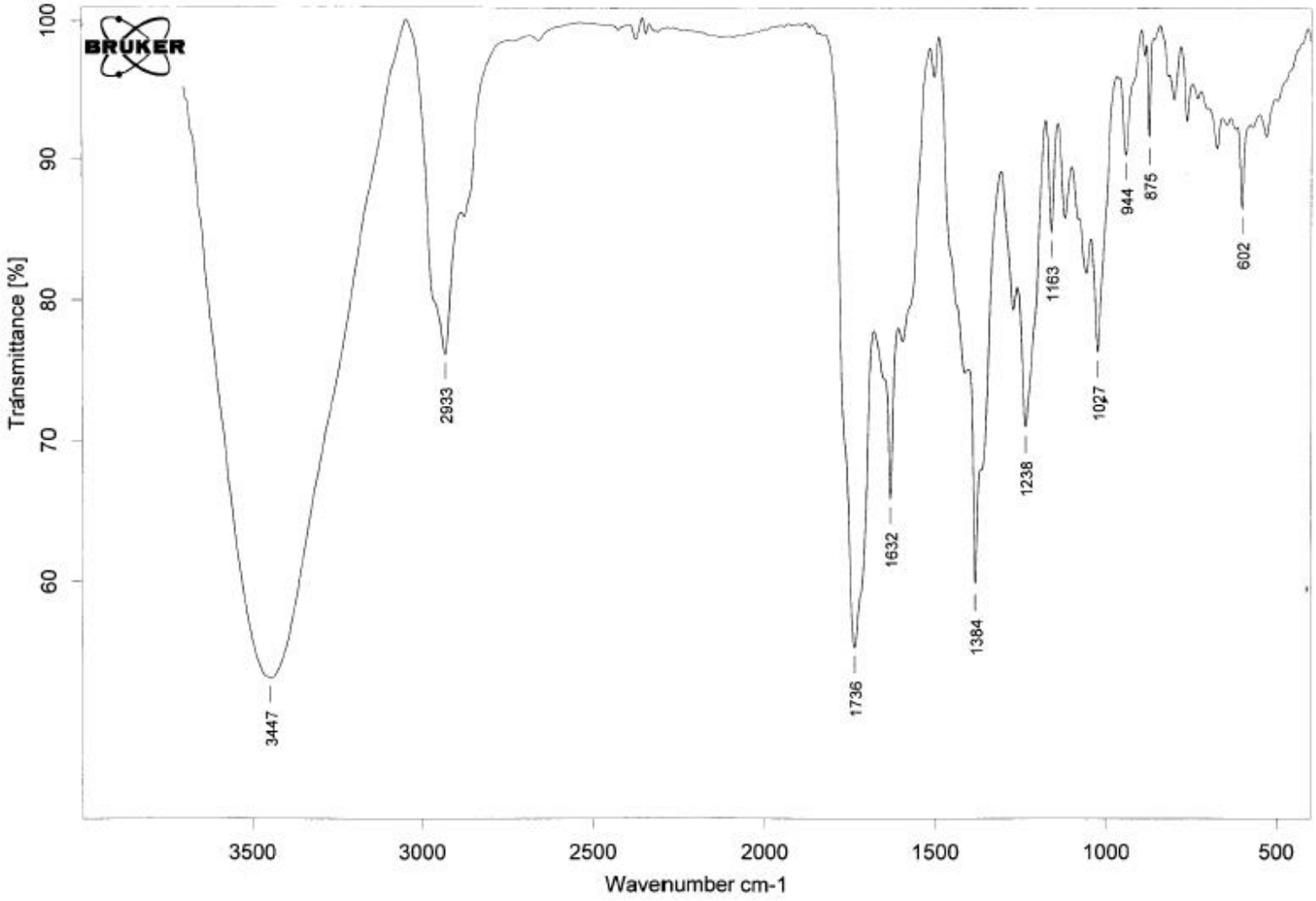
A Segment of NOESY Spectrum of xylogranatin G (**2**) in $CDCl_3$



A Segment of NOESY Spectrum of xylogranatin G (**2**) in $CDCl_3$



IR spectrum of xylogranatin H (**3**)



HR-TOFMS of xylogranatin H (**3**)

Elemental Composition Report

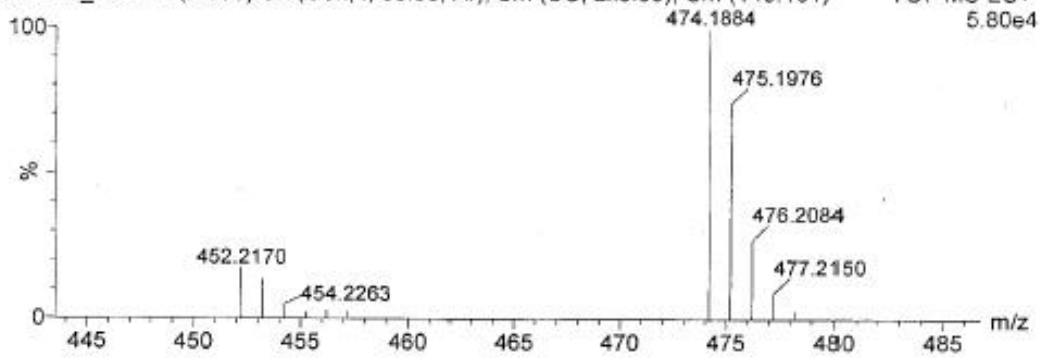
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
49 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

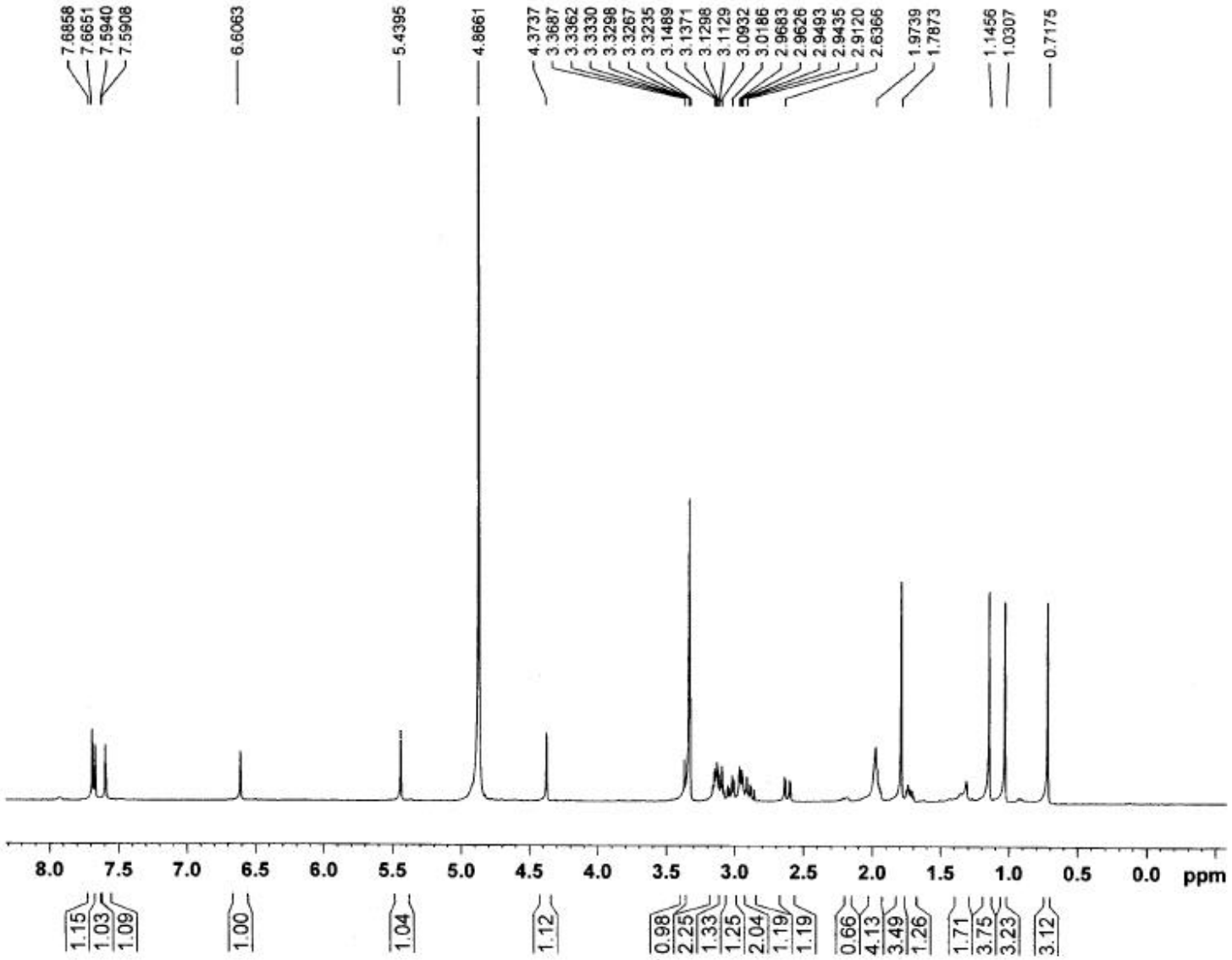
Minimum:				-1.5		
Maximum:		200.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
474.1884	474.1893	-0.9	-1.8	12.5	2	C26 H29 N O6 23Na
	474.1917	-3.3	-6.9	15.5	1	C28 H28 N O6

Wu08

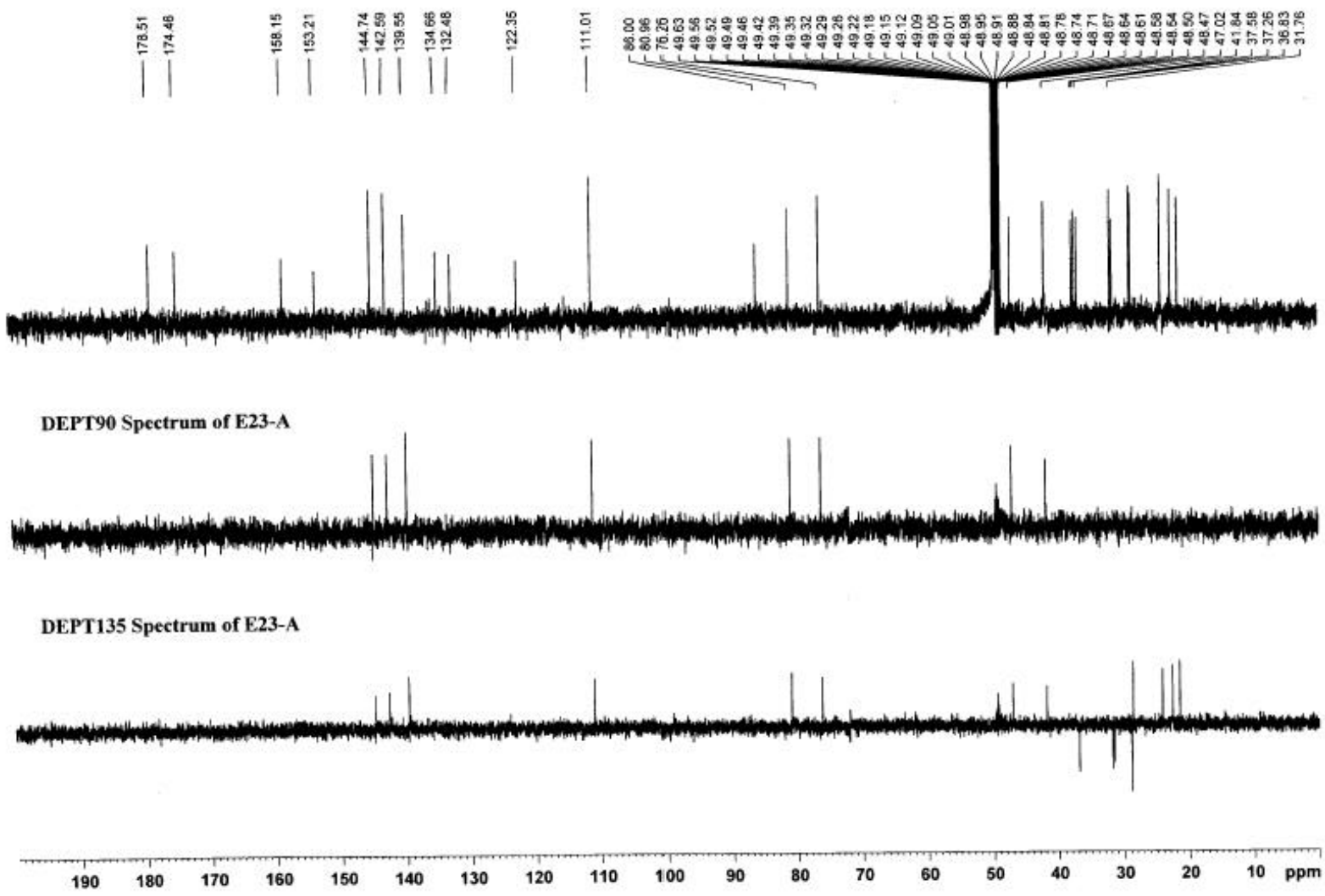
060929_05 141 (2.699) Cn (Cen,4, 80.00, Ar); Sm (SG, 2x3.00); Cm (140:151) TOF MS ES+ 5.80e4



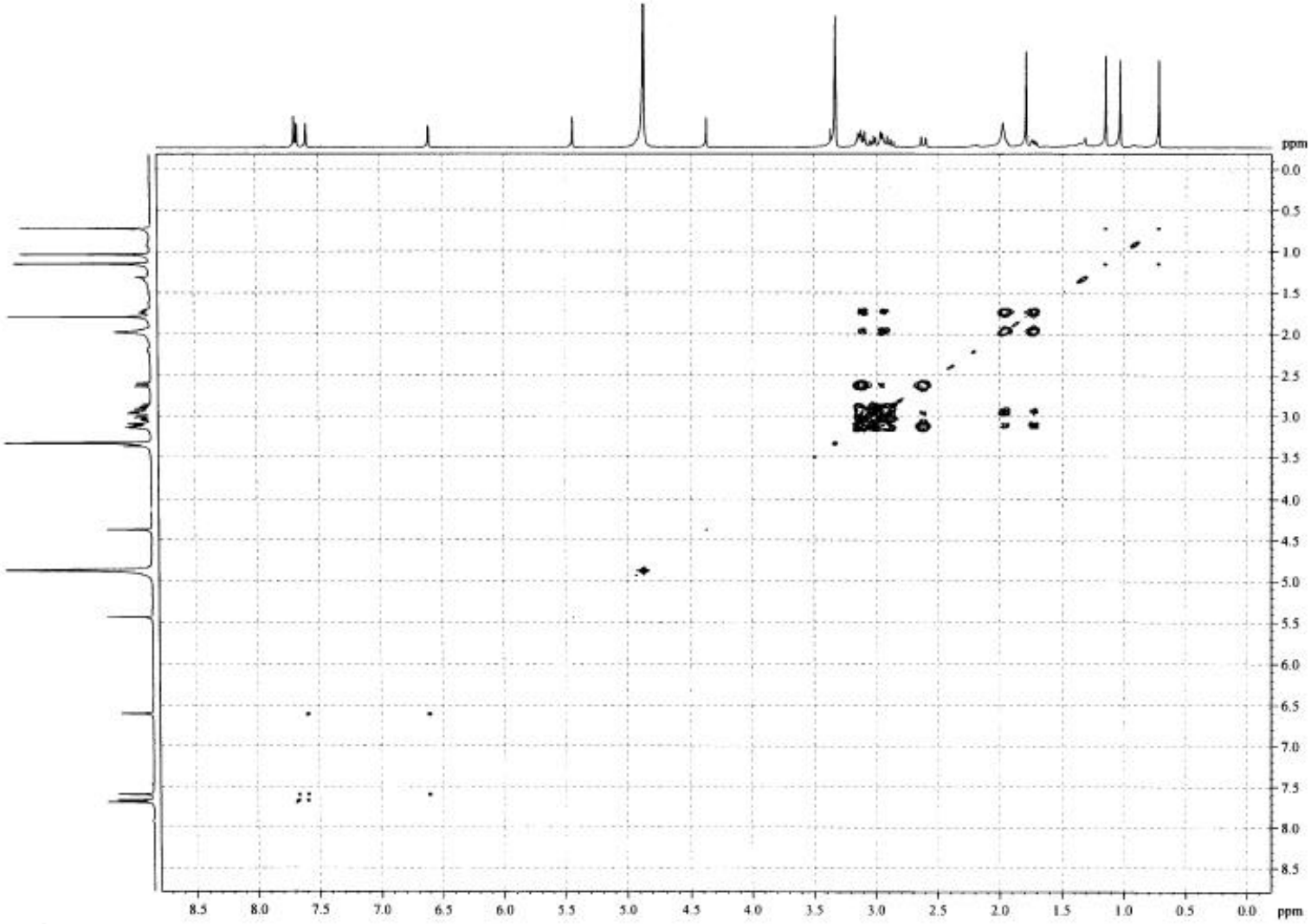
^{1}H NMR (500 MHz) Spectrum of xylogranatin H (**3**) in methanol-d_4



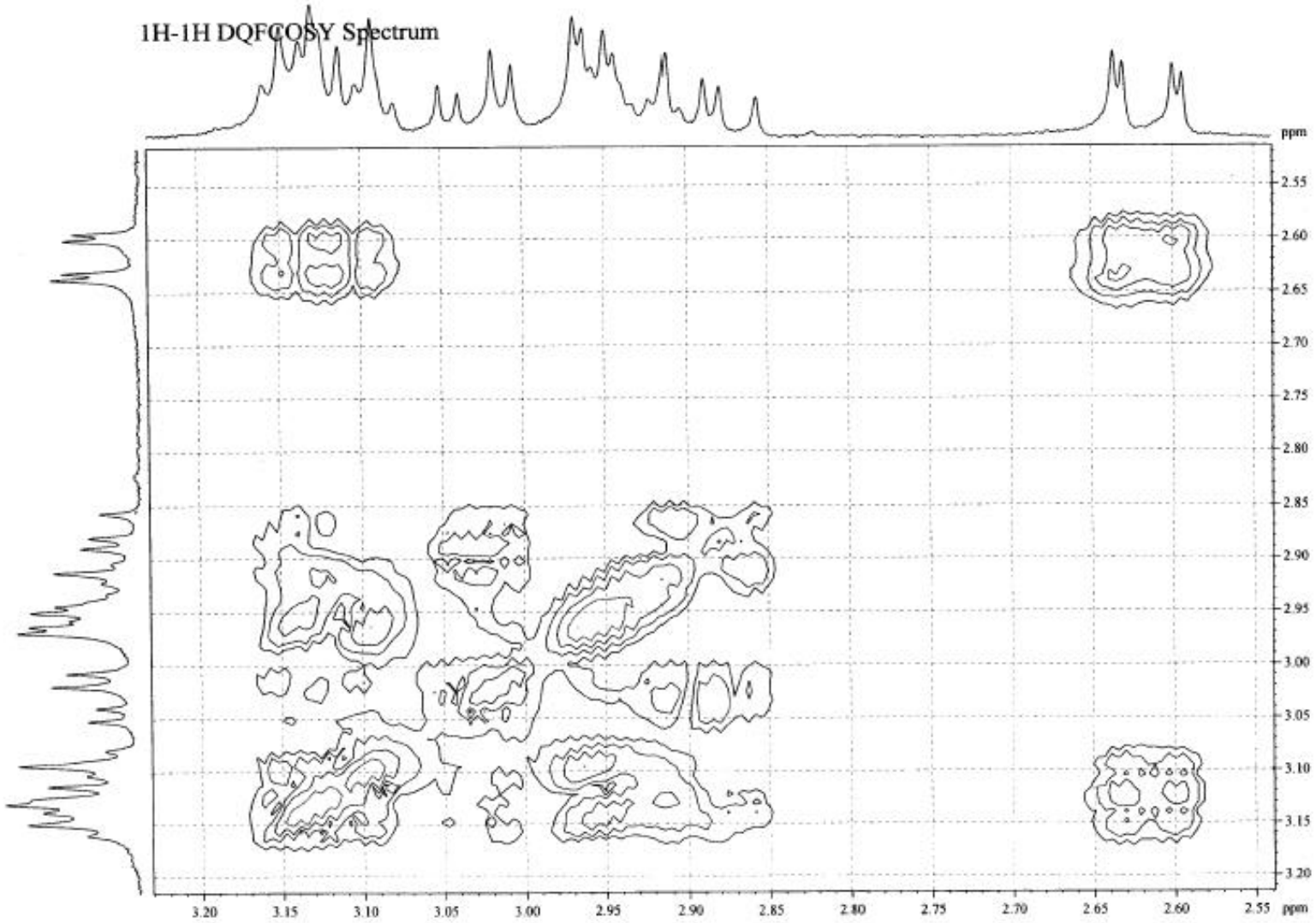
^{13}C NMR (125 MHz) Spectrum and DEPT experiments of xylogranatin H (**3**) in methanol-d_4



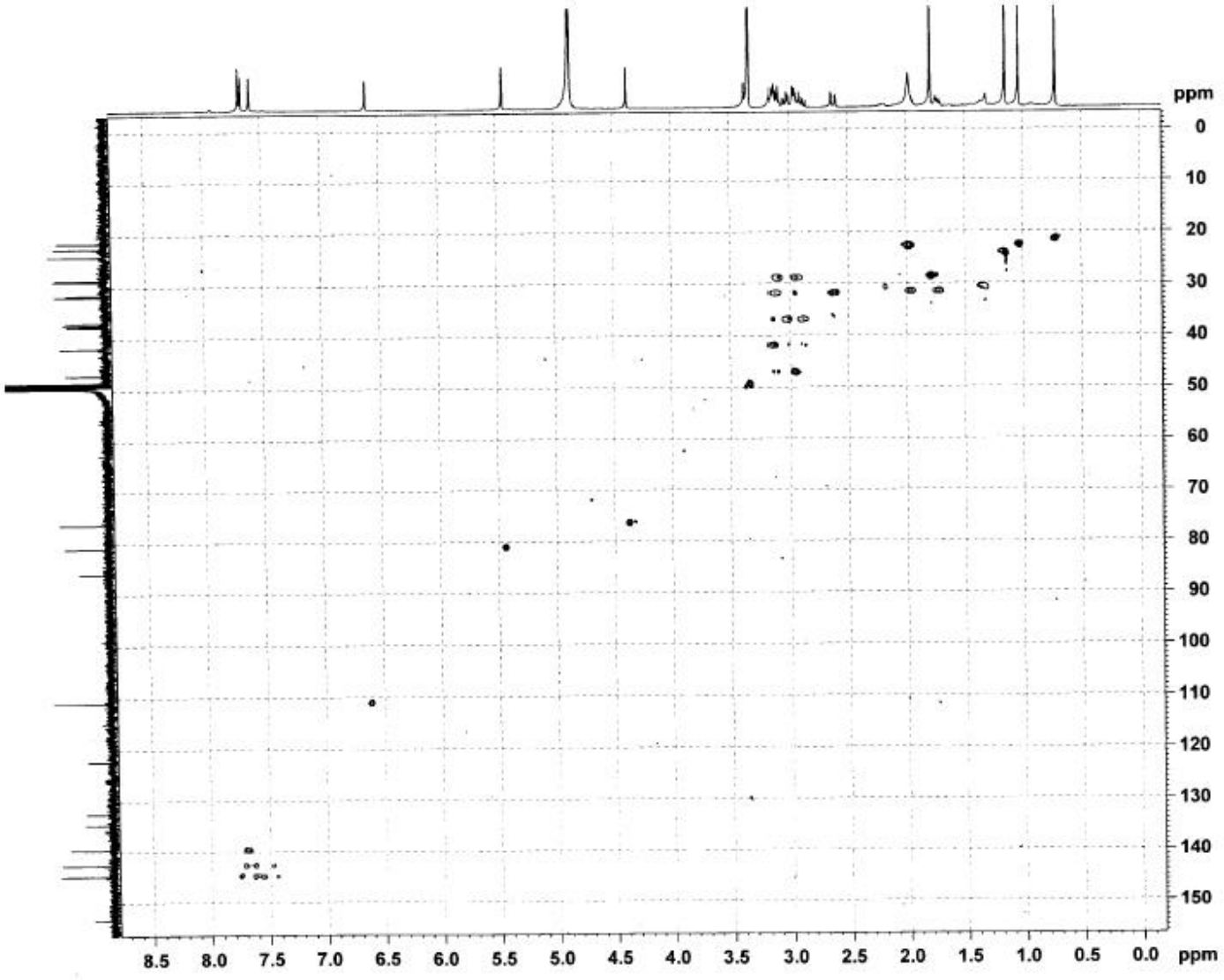
^{1}H-^{1}H COSY Spectrum of xylogranatin H (**3**) in methanol-d_4



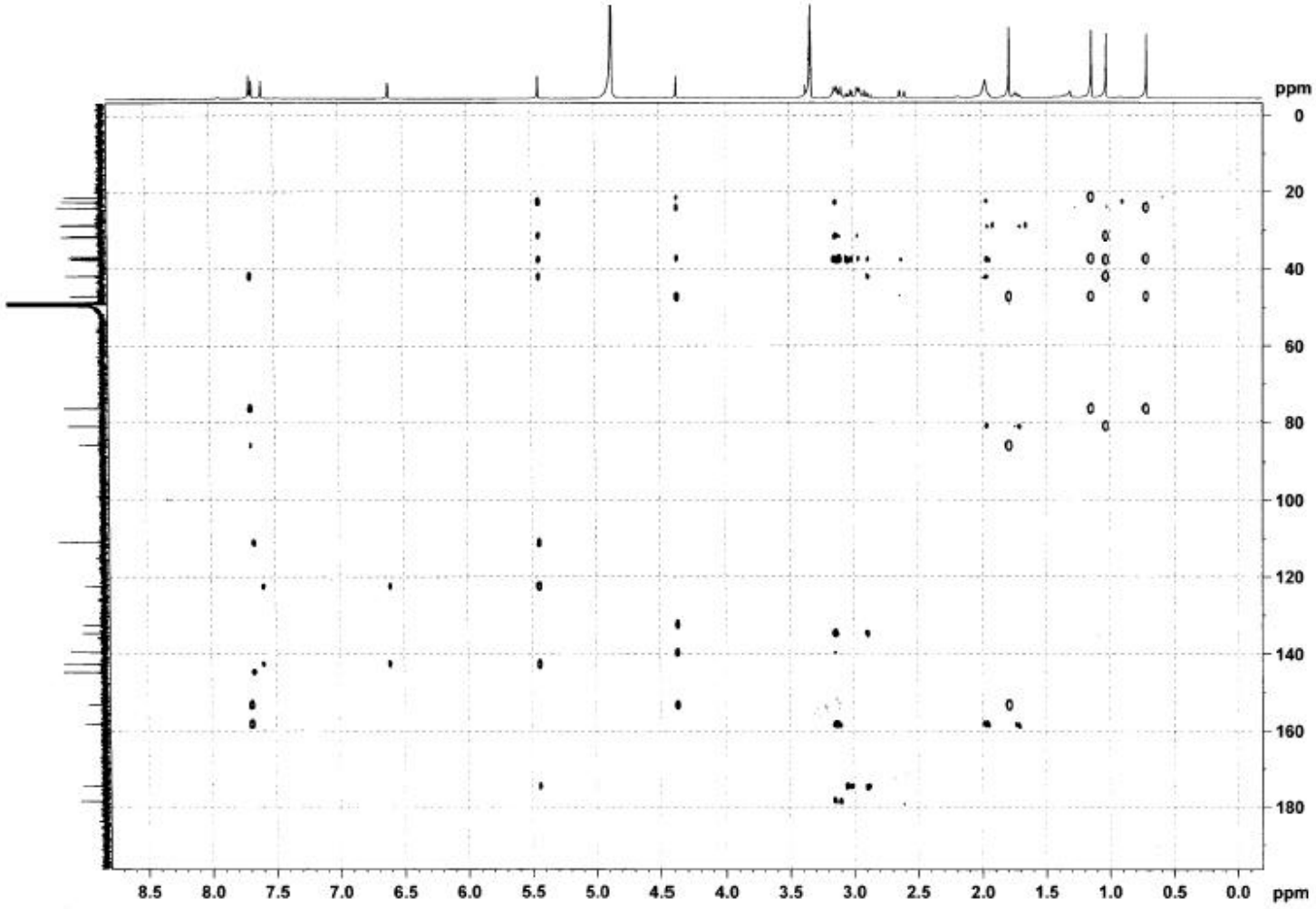
A Segment of ^{1}H-^{1}H COSY Spectrum of xylogranatin H (**3**) in methanol-d_4



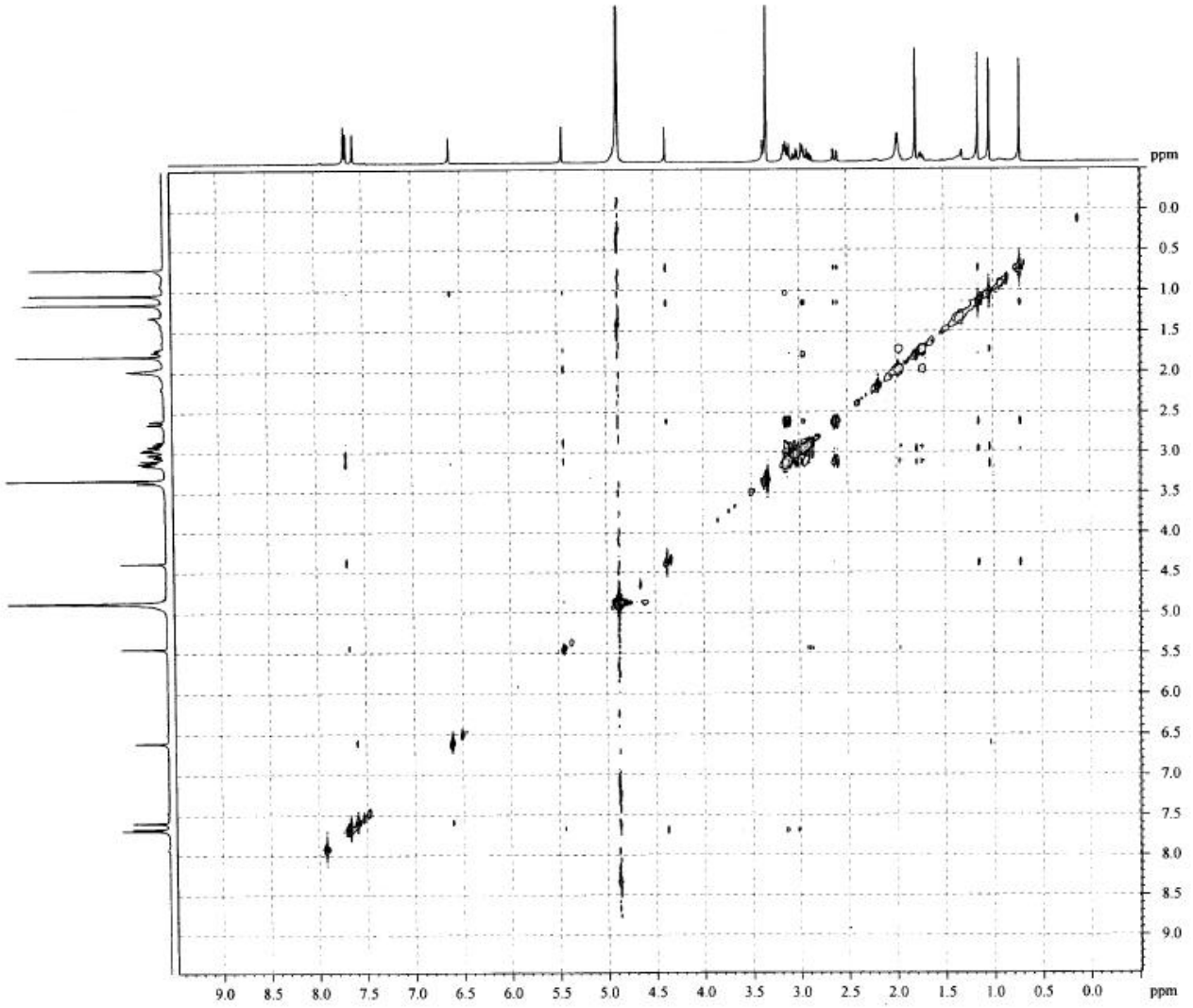
HSQC Spectrum of xylogranatin H (**3**) in methanol-d_4



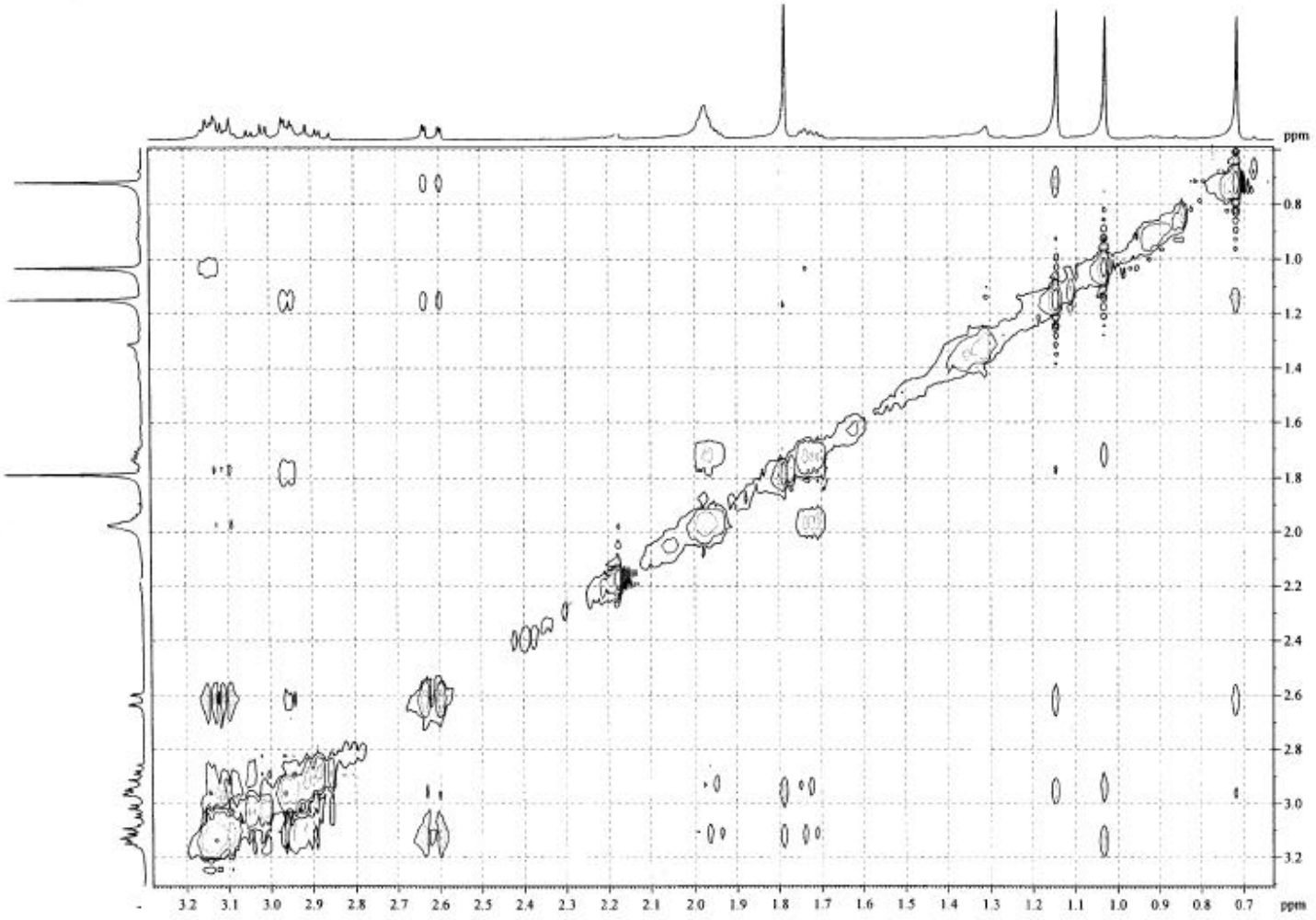
HMBC Spectrum of xylogranatin H (**3**) in methanol-d_4



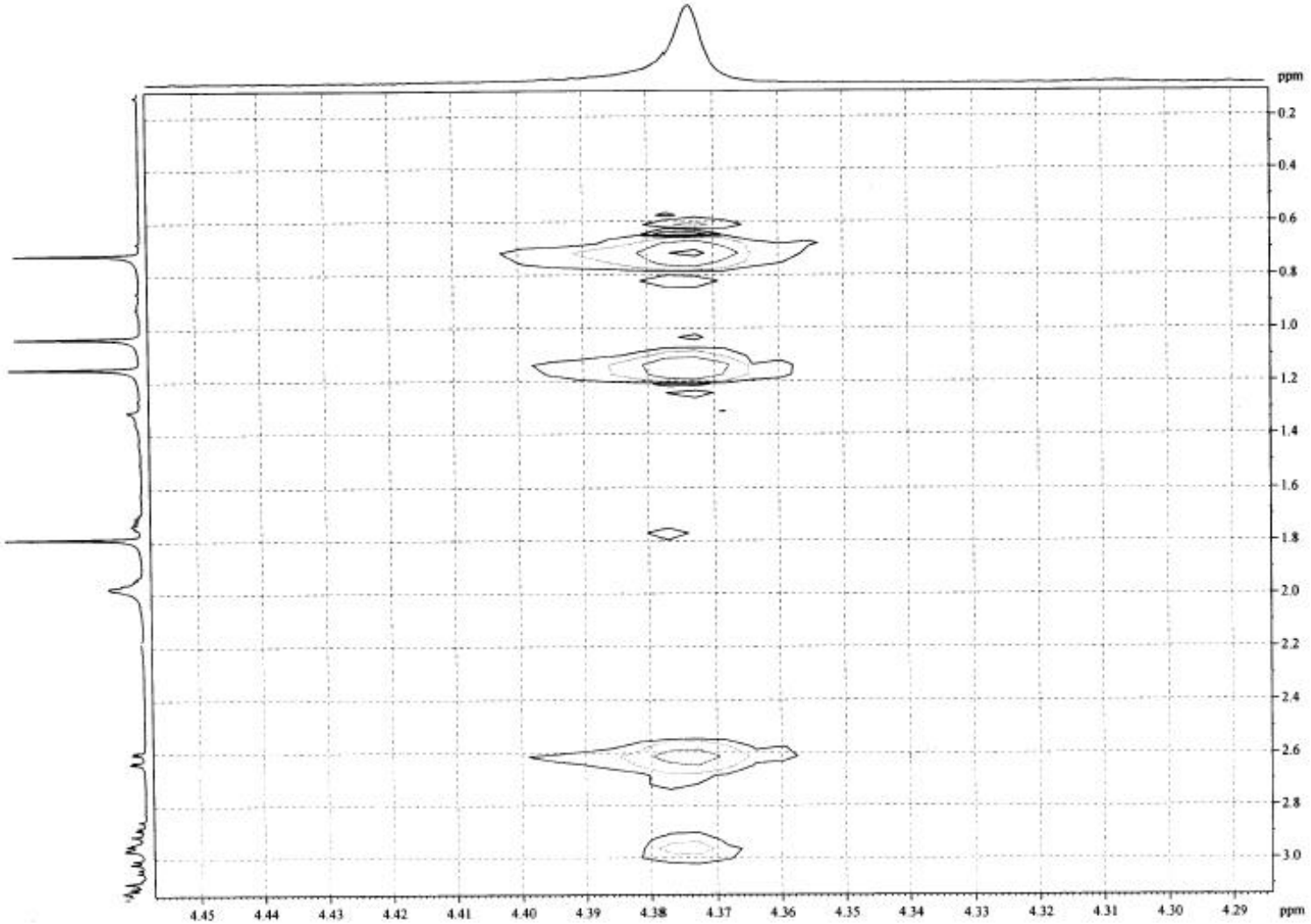
NOESY Spectrum of xylogranatin H (**3**) in methanol-d_4



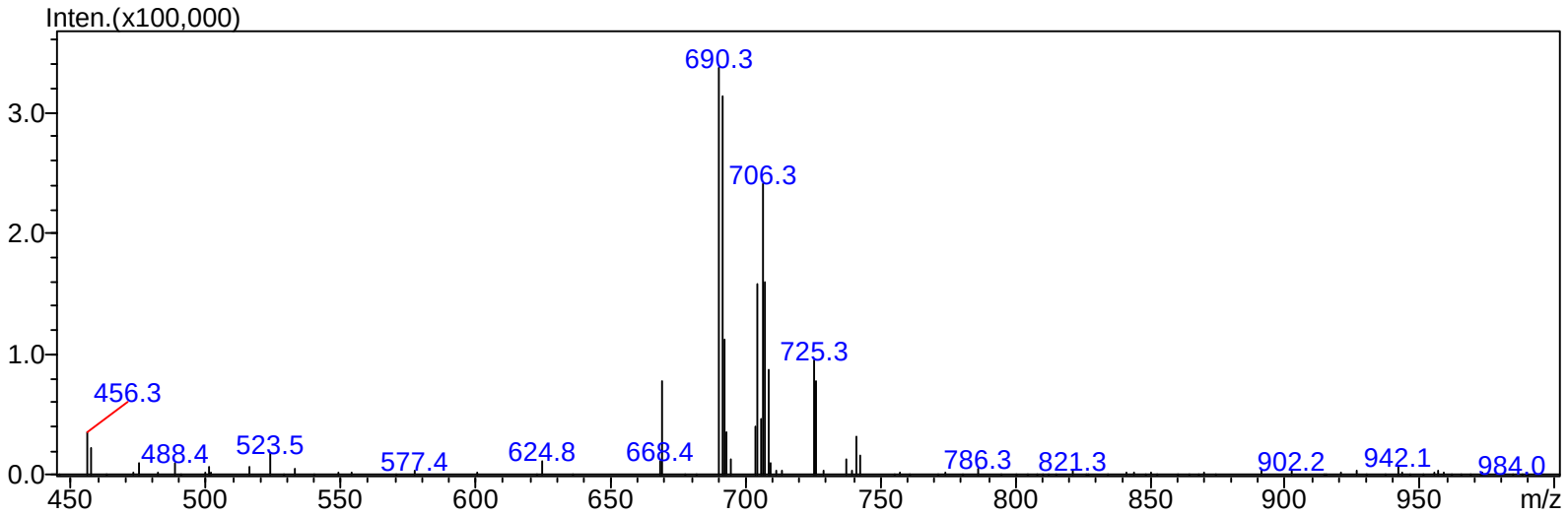
A Segment of NOESY Spectrum of xylogranatin H (**3**) in methanol-d_4



A Segment of NOESY Spectrum of xylogranatin H (**3**) in methanol-d_4



ESI-MS of **3s**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3.0
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1.0
0.0
690.3
706.3
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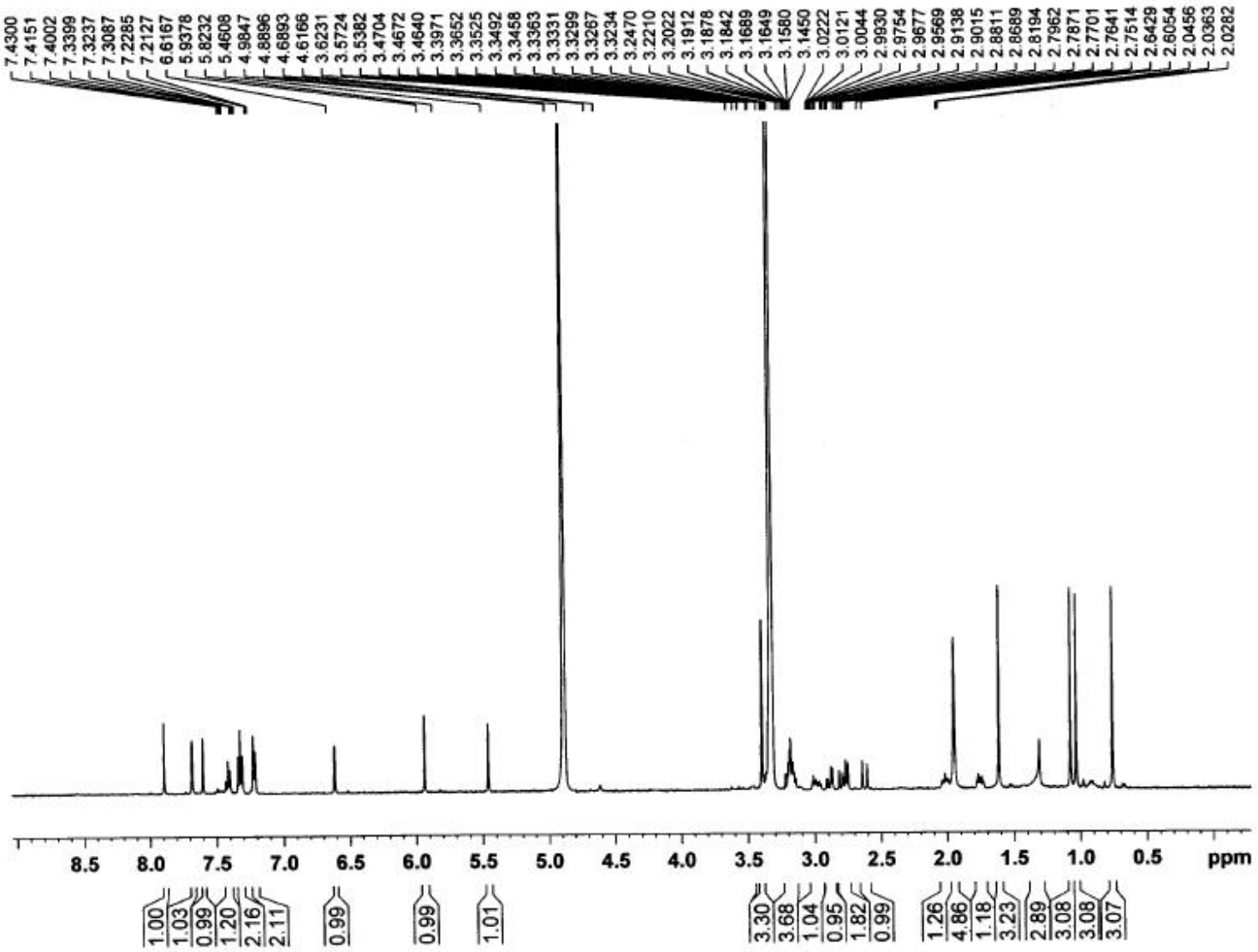
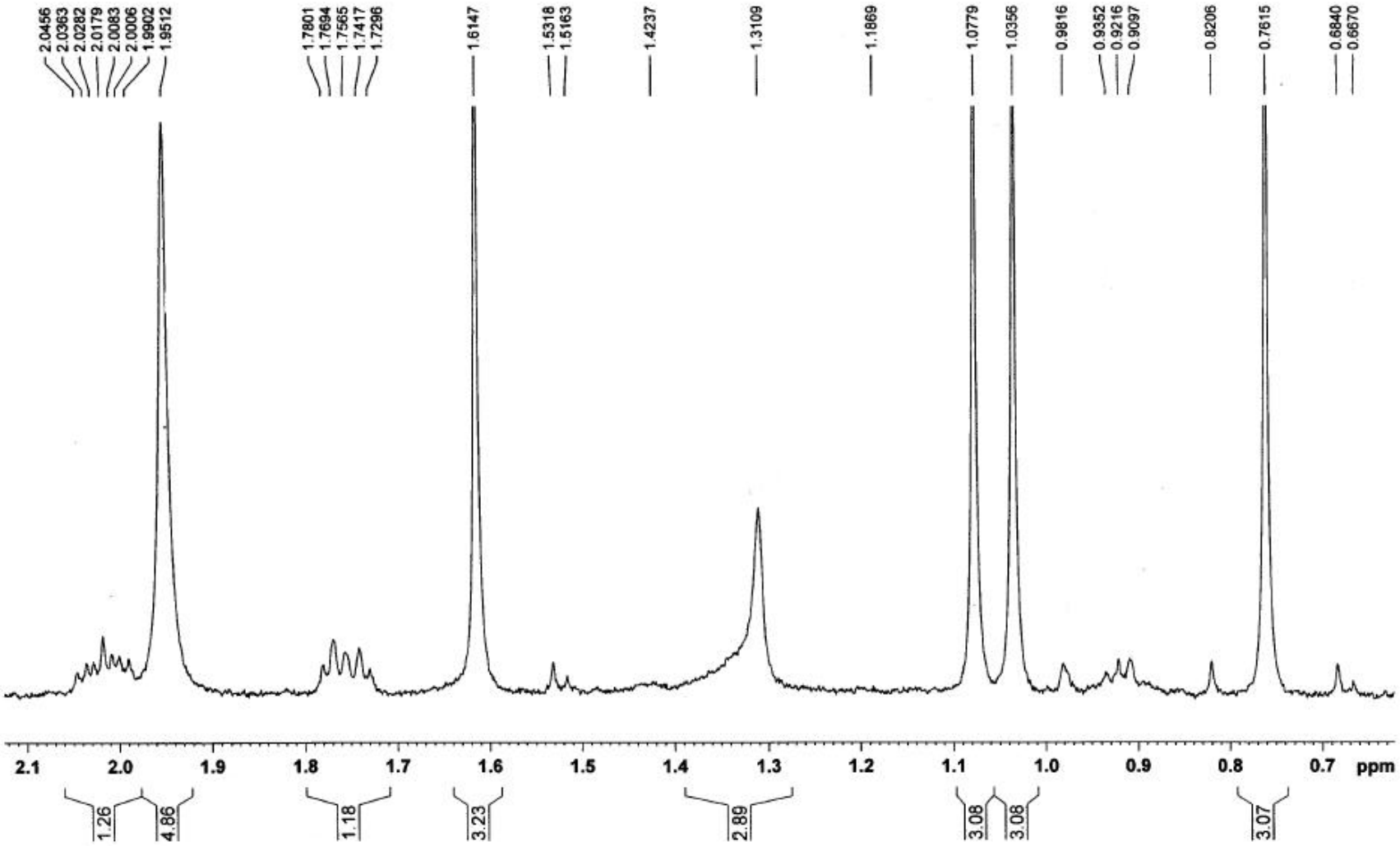
456.3
488.4
523.5
577.4
624.8
668.4
786.3
821.3
902.2
942.1
984.0
450
500
550
600
650
700
750
800
850
900
950
m/z

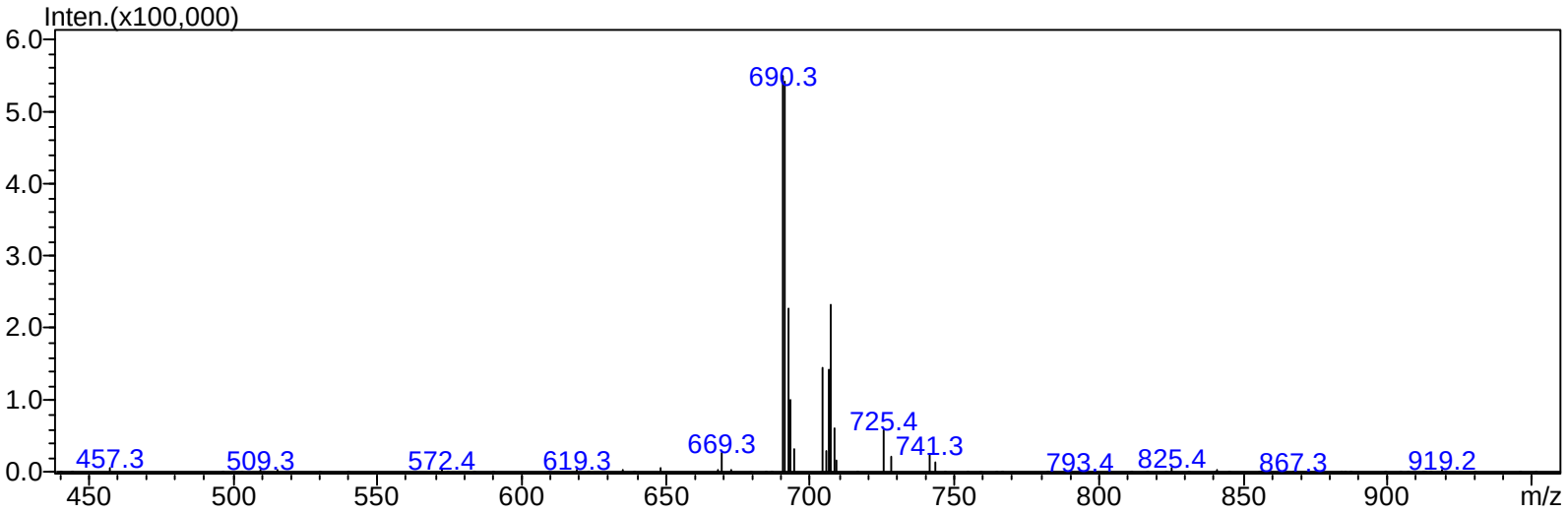
^{1}H NMR (500 MHz) of **3s** in methanol-d_4



A Segment of ^{1}H NMR (500 MHz) of **3s** in methanol-d_4



ESI-MS of **3r**


Inten.(x100,000)
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669.3
741.3
457.3
509.3
572.4
619.3
793.4
825.4
867.3
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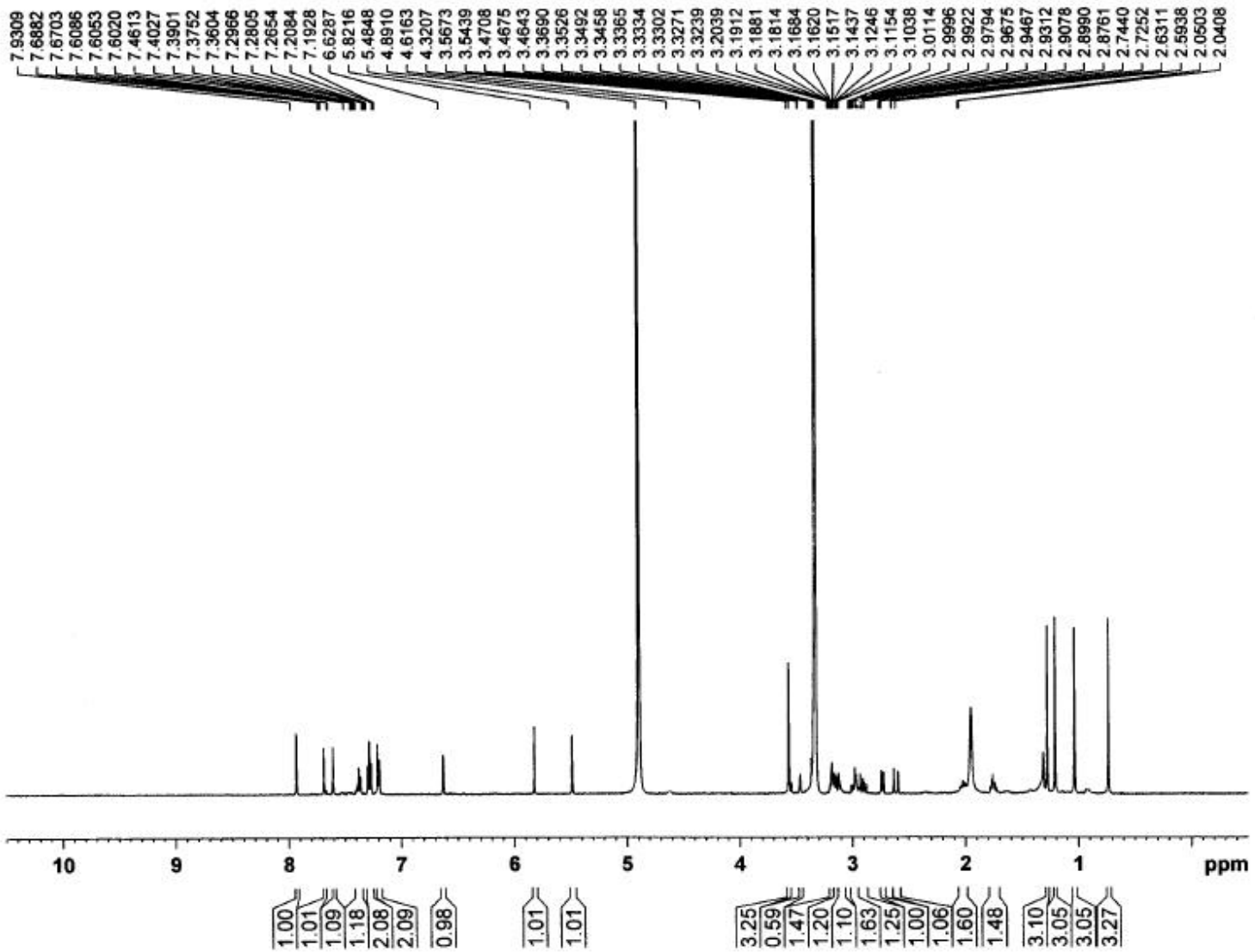
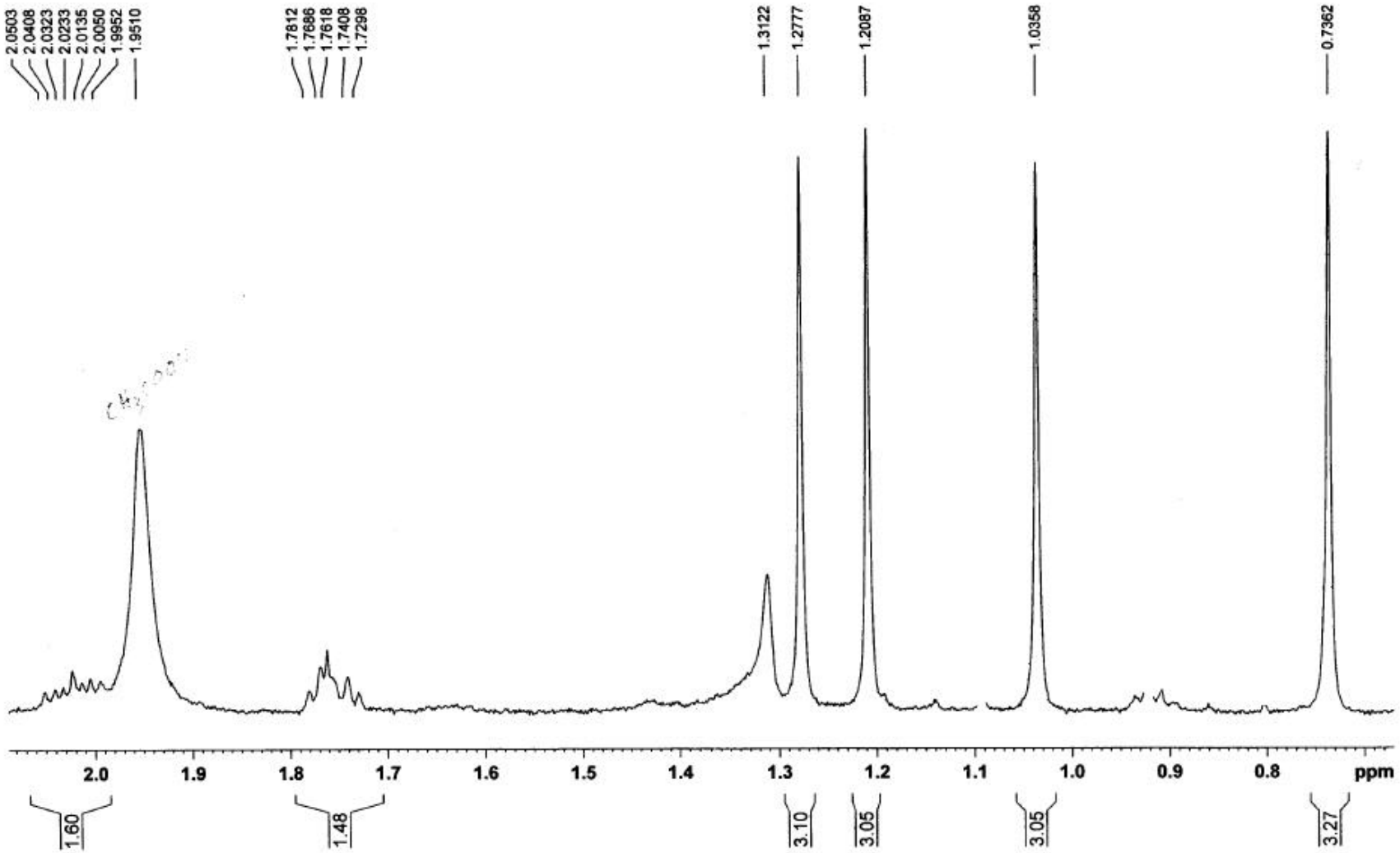
450
500
550
600
650
700
750
800
850
900
m/z

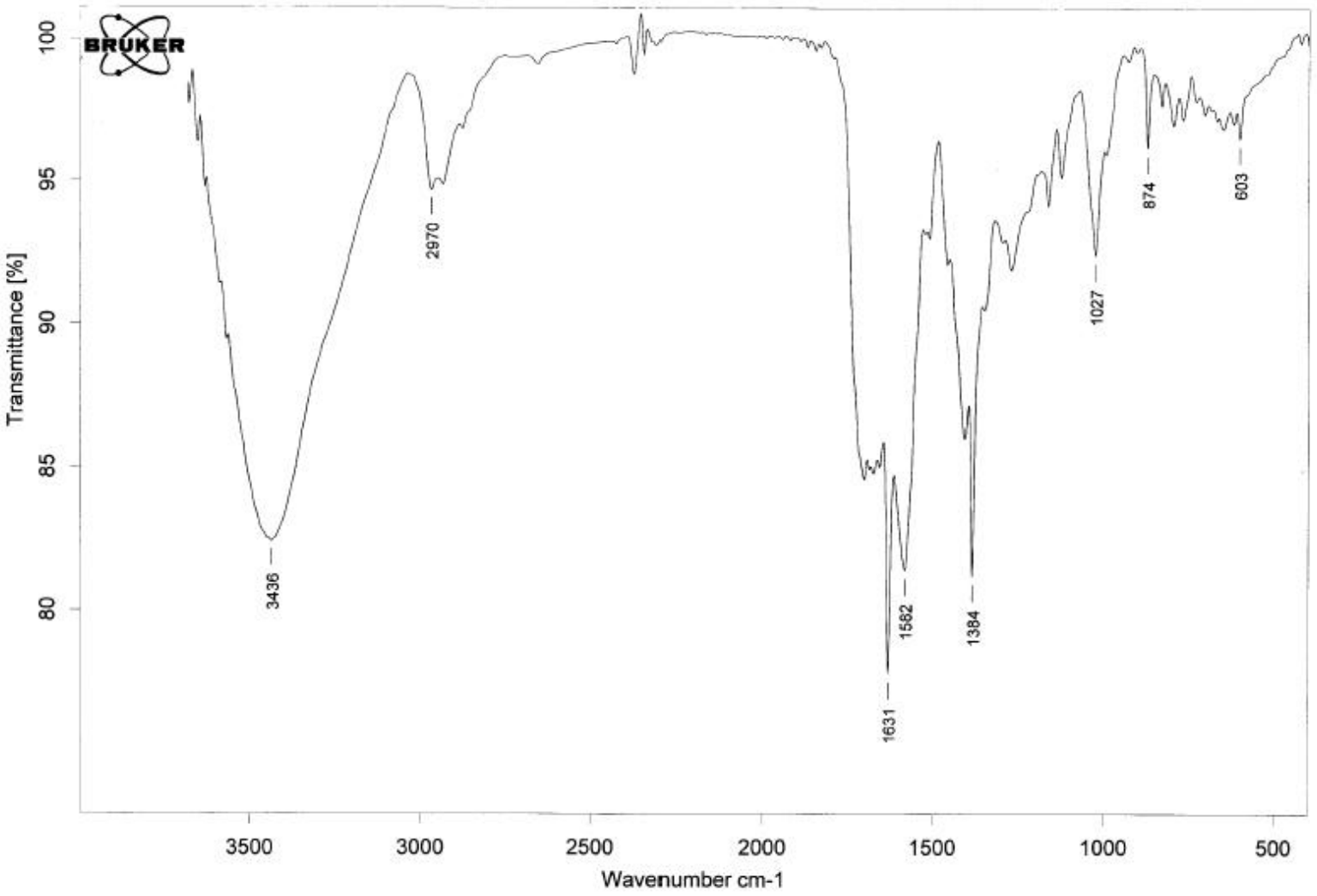
^{1}H NMR (500 MHz) of **3r** in methanol-d_4



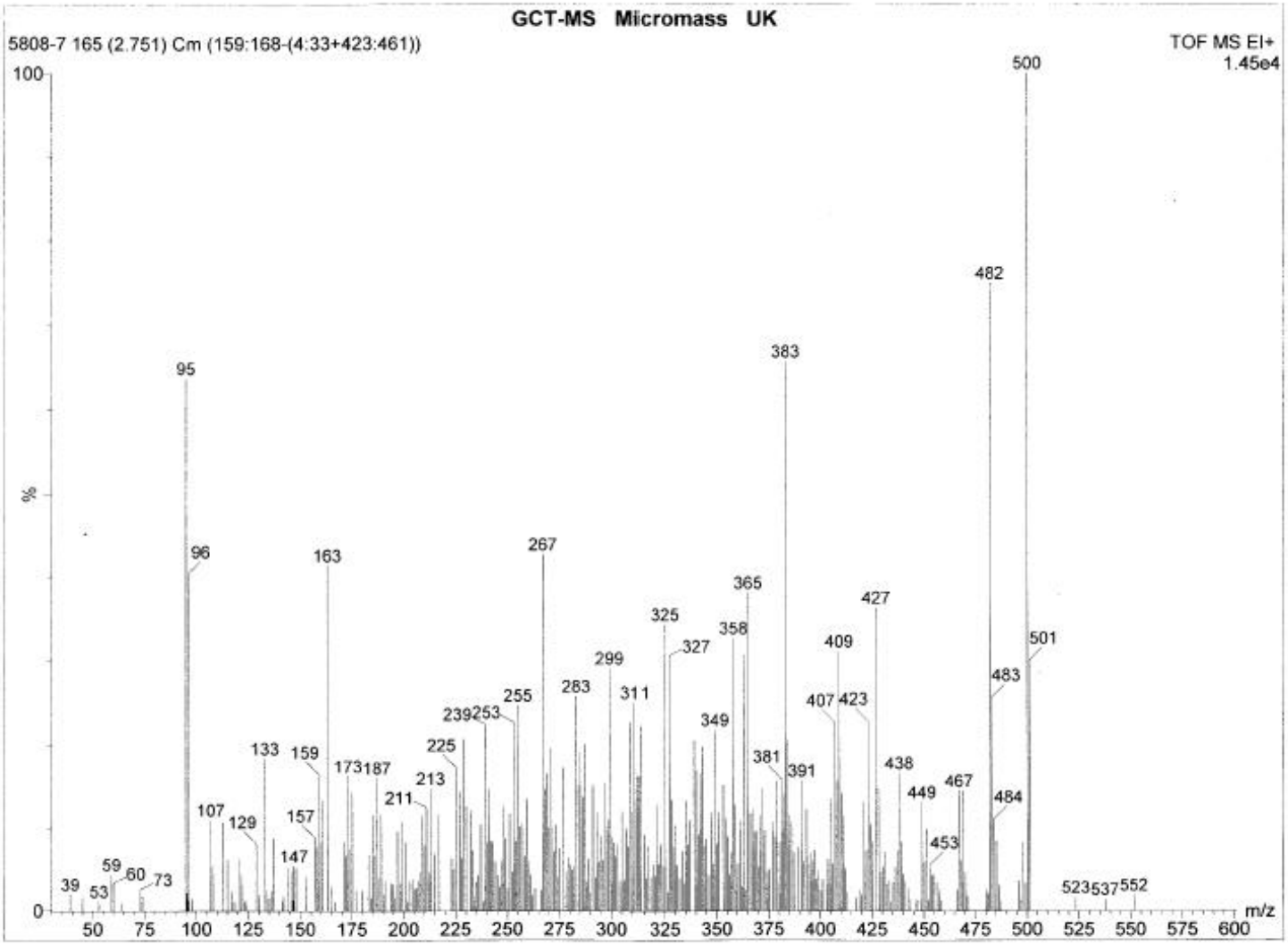
A Segment of ^{1}H NMR (500 MHz) of **3r** in methanol-d_4



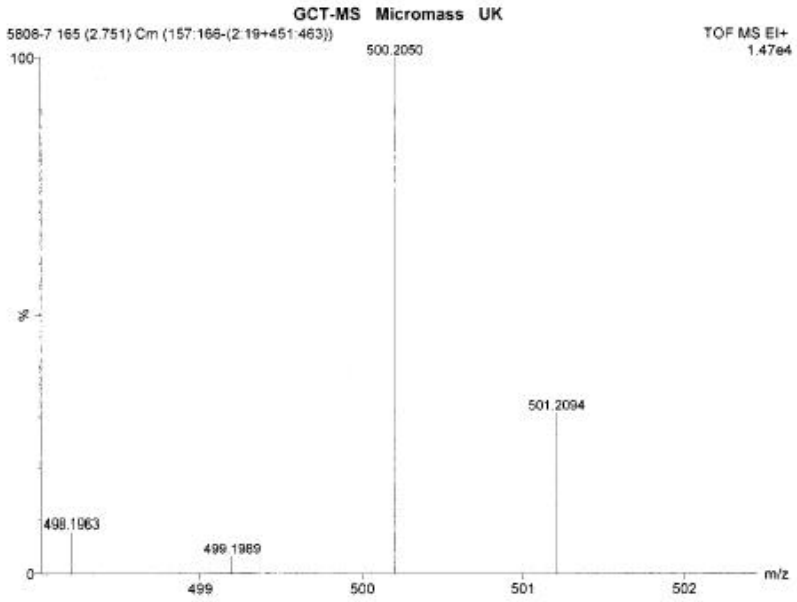
IR spectrum of xylogranatin I (**4**)



TOFMS of xylogranatin I (**4**)



HR-TOFMS of xylogranatin I (**4**)



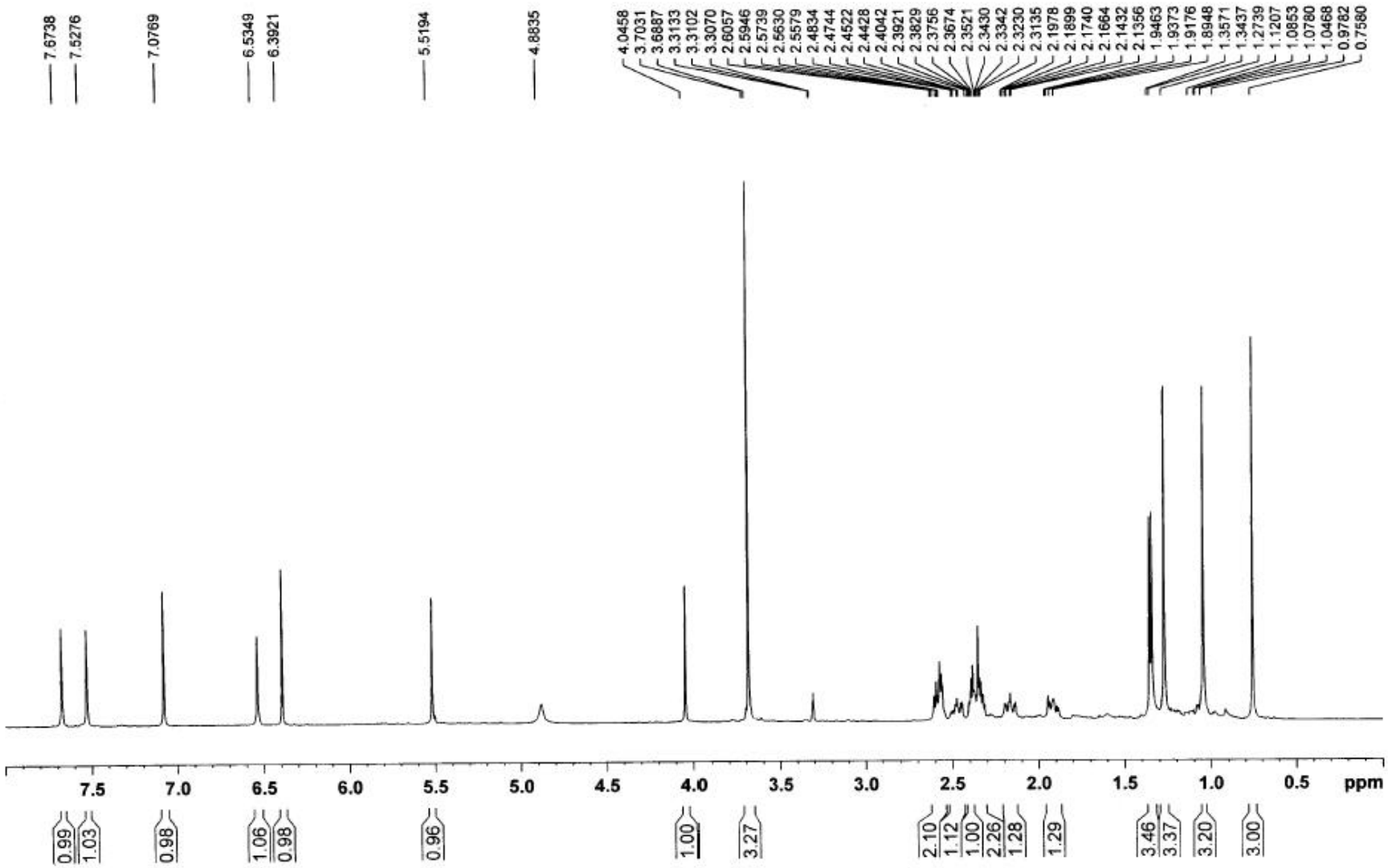
Elemental Composition Report

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

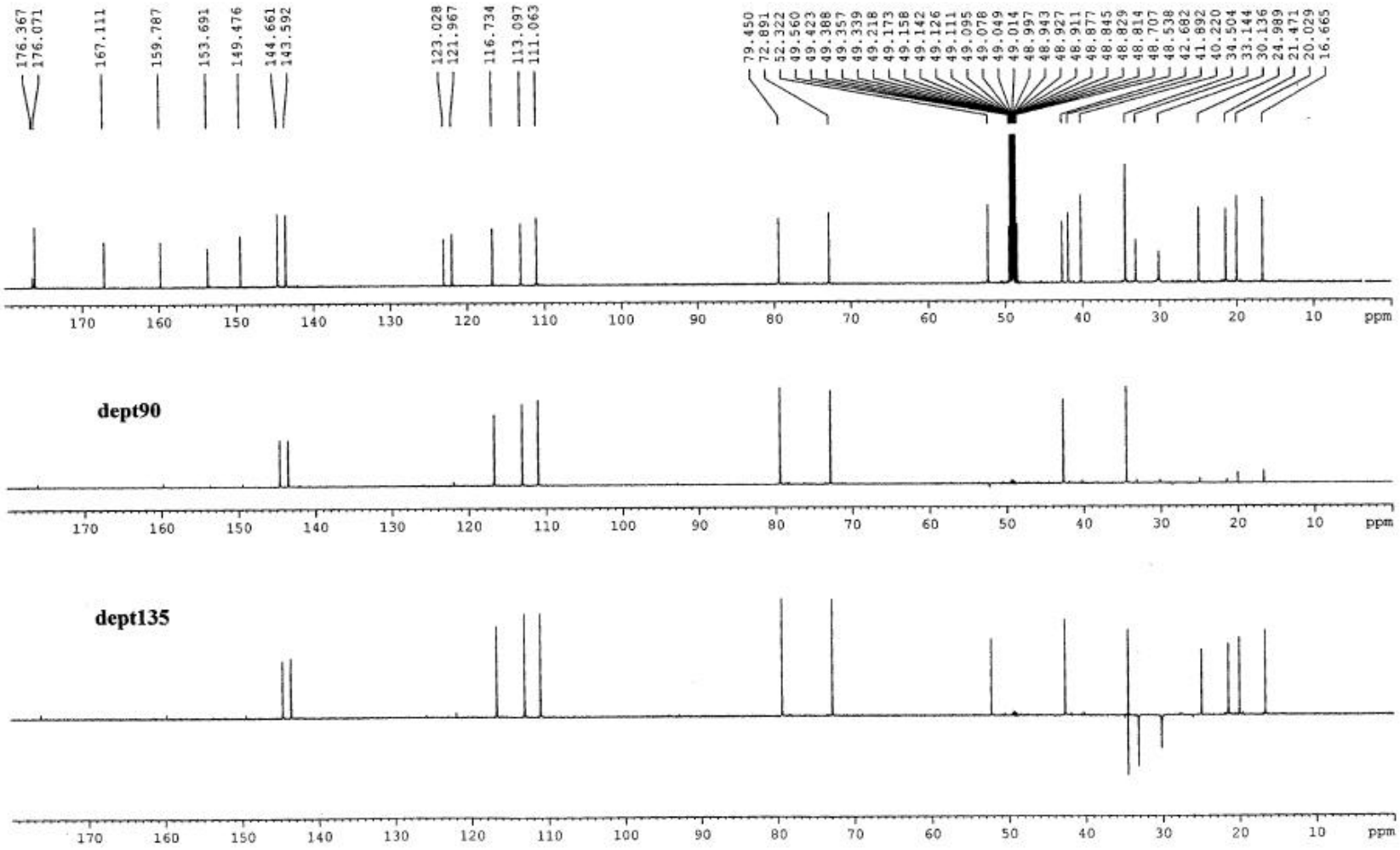
Monoisotopic Mass, Odd and Even Electron Ions
69 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Minimum:	80.00				-1.5		
Maximum:	100.00		3.0	5.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
500.2050	100.00	500.2046	0.4	0.7	12.0	1	C27 H32 O9

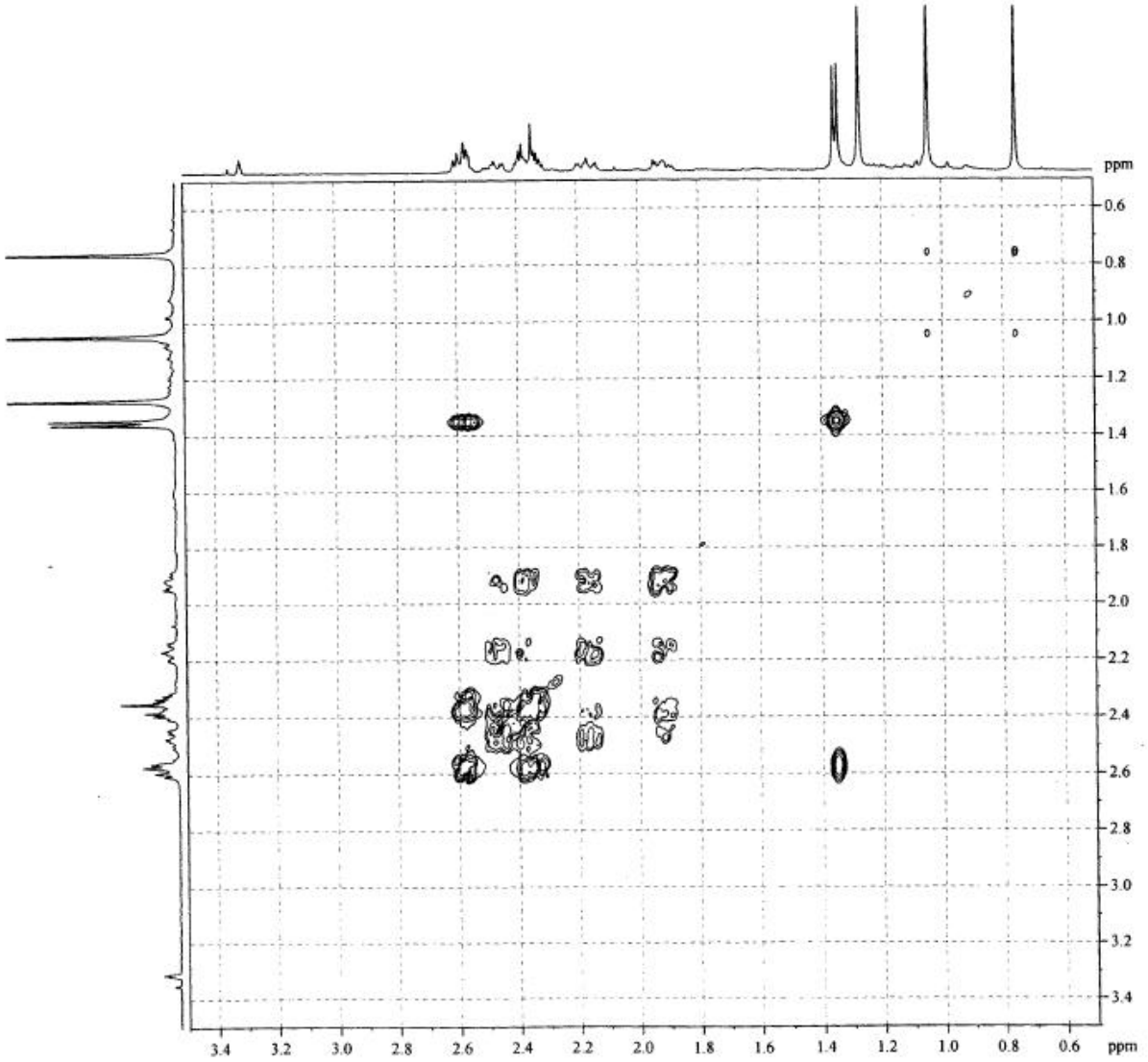
^{1}H NMR (500 MHz) Spectrum of xylogranatin I (**4**) in methanol-d_4



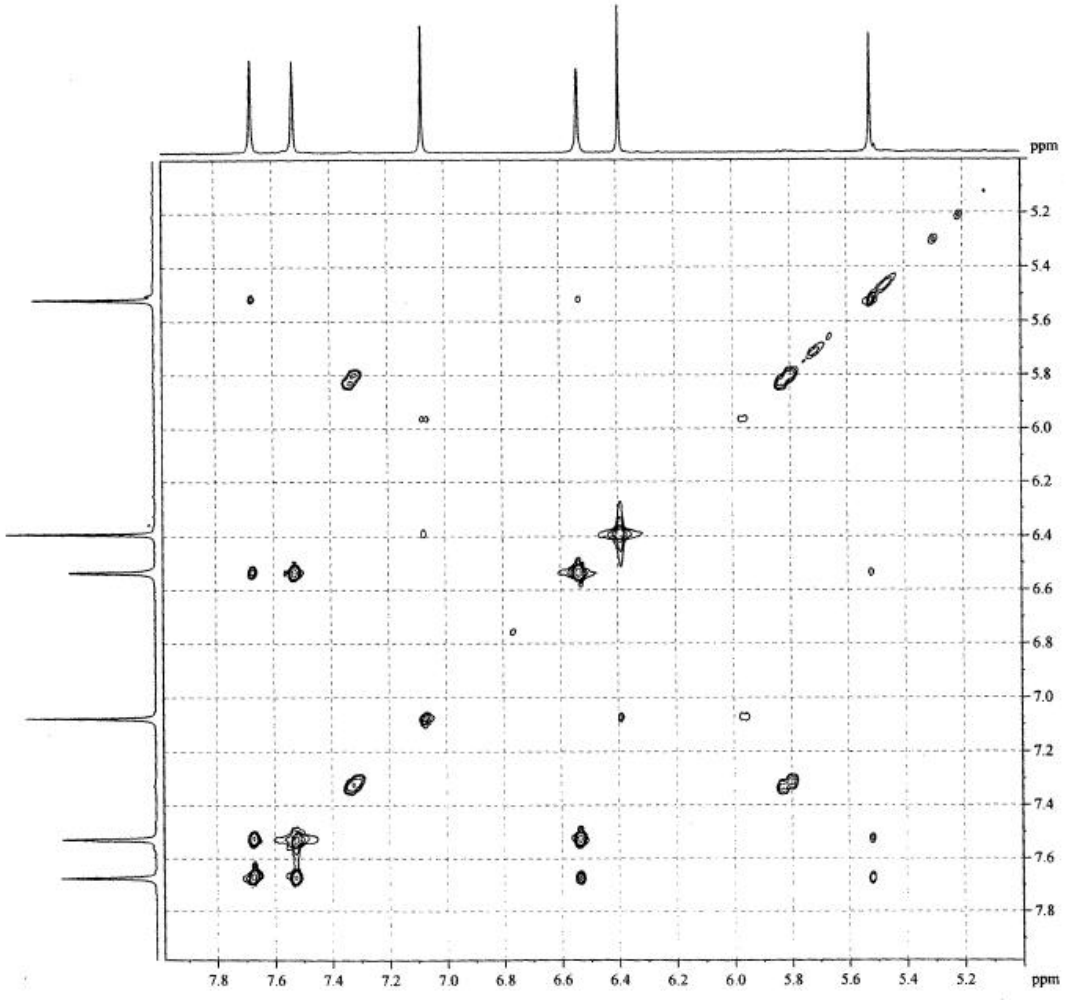
^{13}C NMR (125 MHz) Spectrum and DEPT experiments of xylogranatin I (**4**) in methanol-d_4



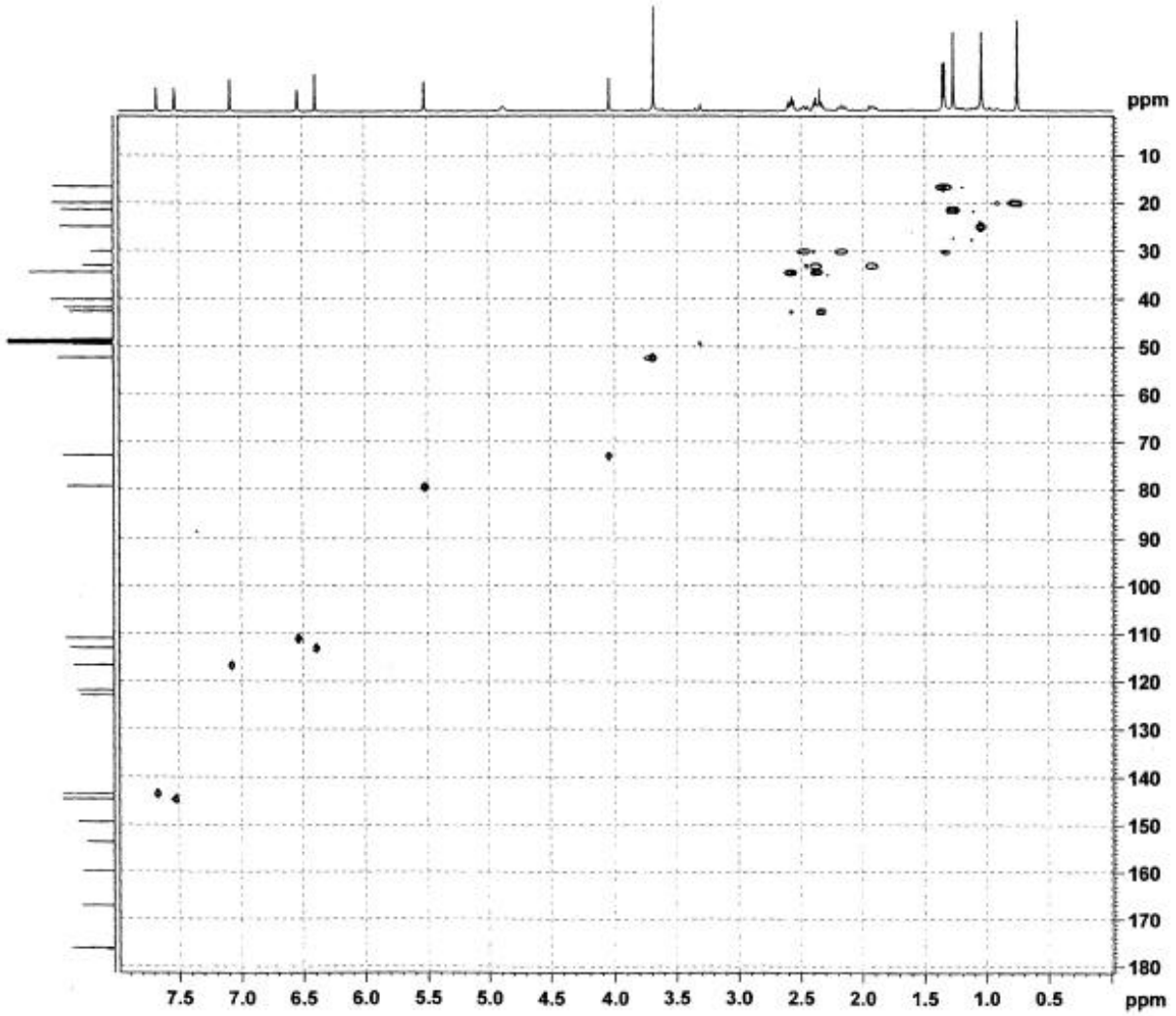
A Segment of ^{1}H-^{1}H COSY Spectrum of xylogranatin I (**4**) in methanol-d_4



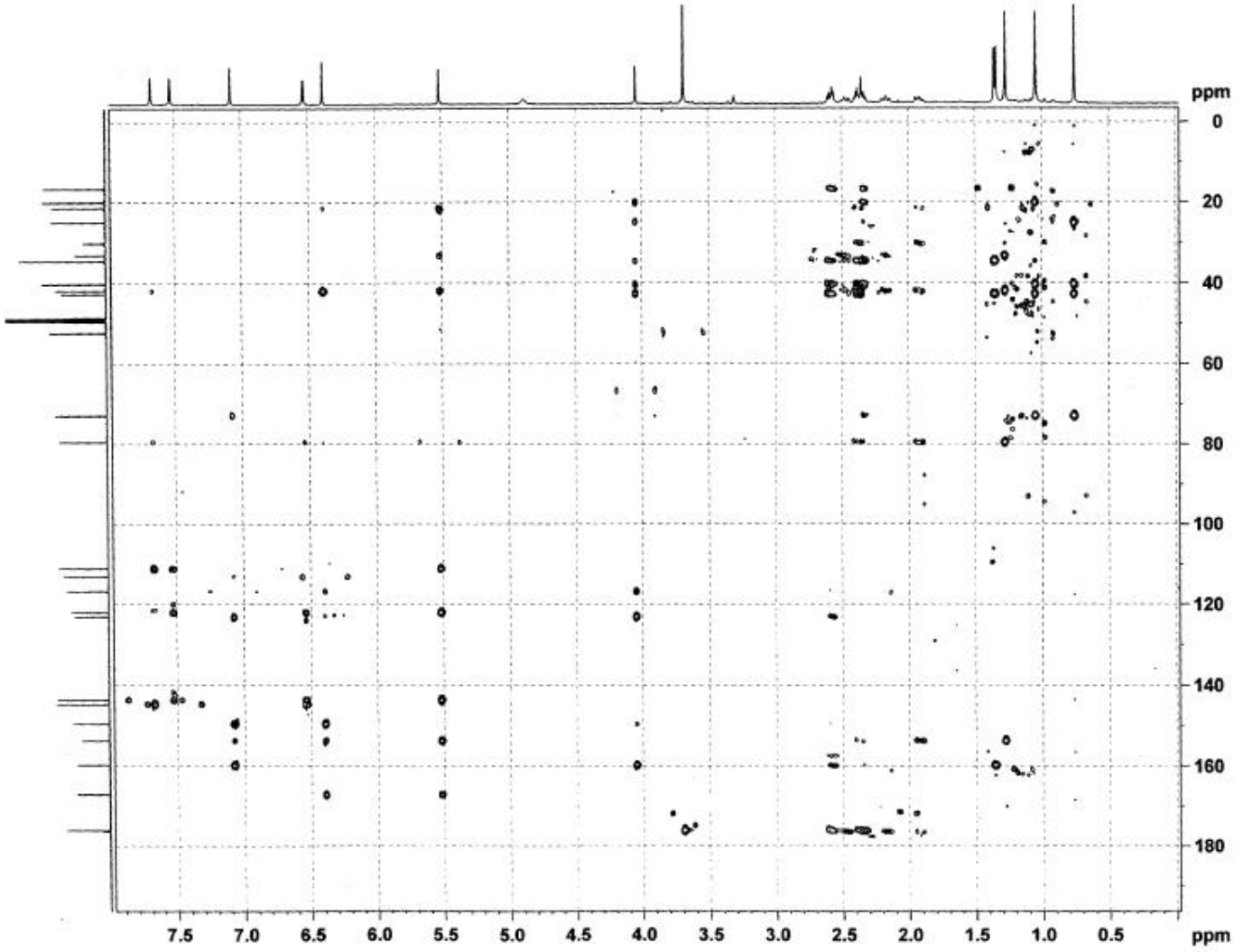
A Segment of ^{1}H-^{1}H COSY Spectrum of xylogranatin I (**4**) in methanol-d_4



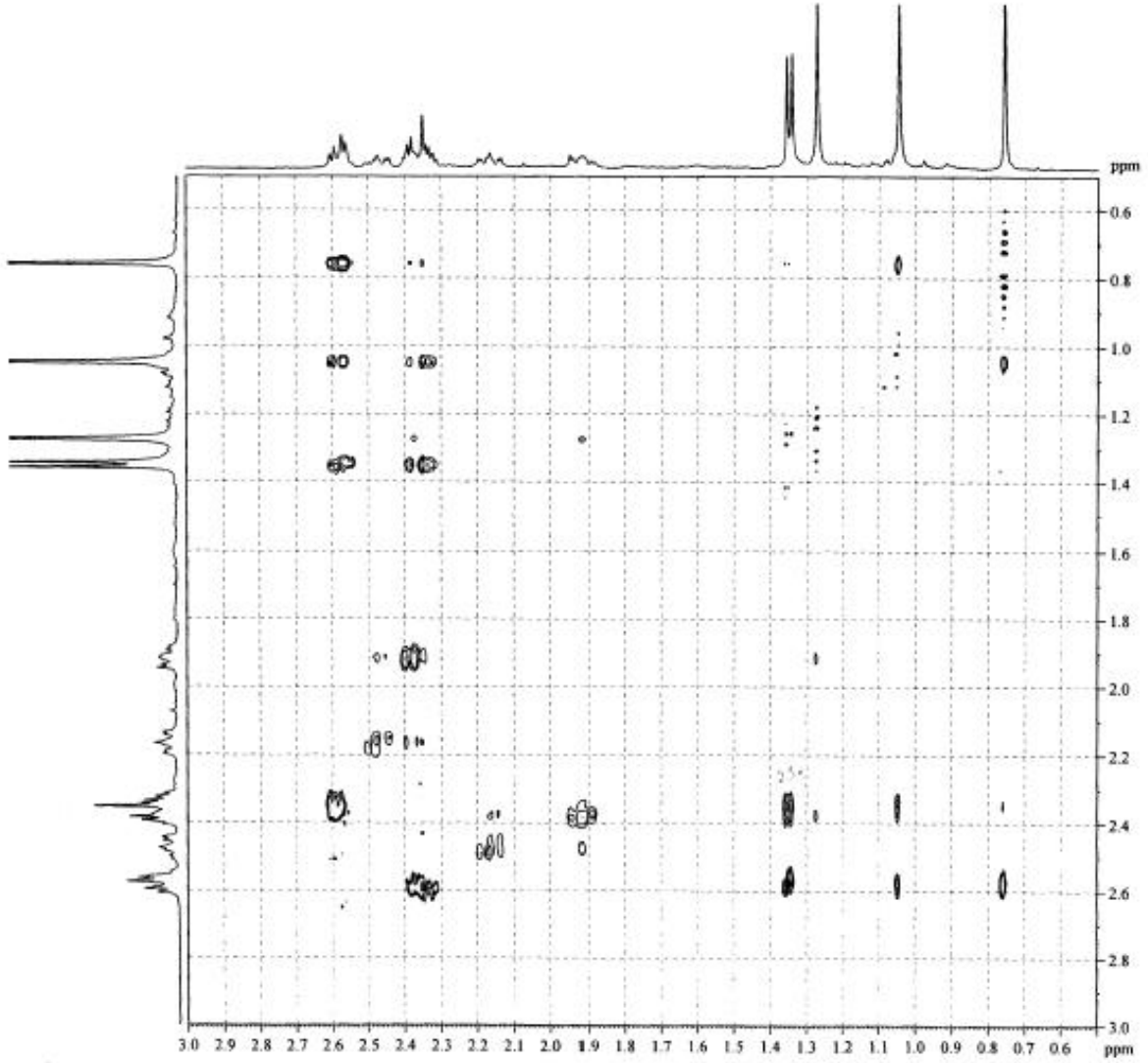
HSQC Spectrum of xylogranatin I (**4**) in methanol-d_4



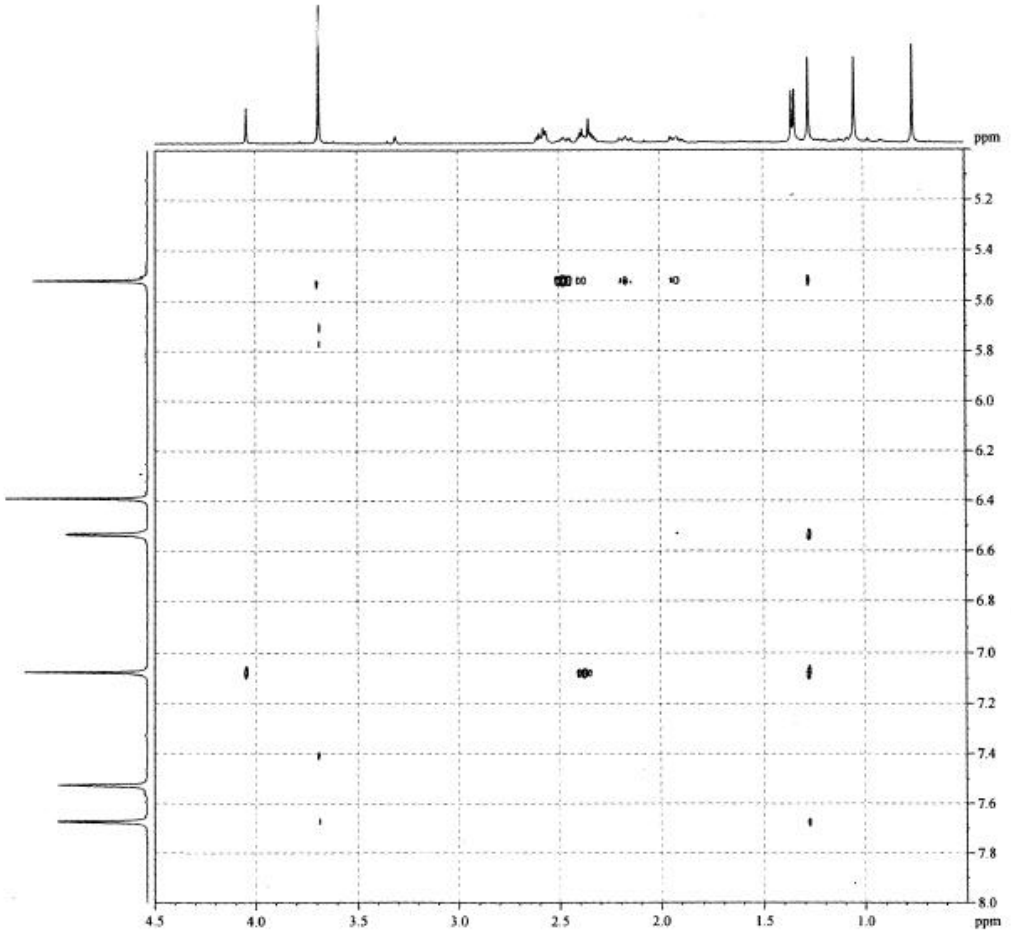
HMBC Spectrum of xylogranatin I (**4**) in methanol-d_4



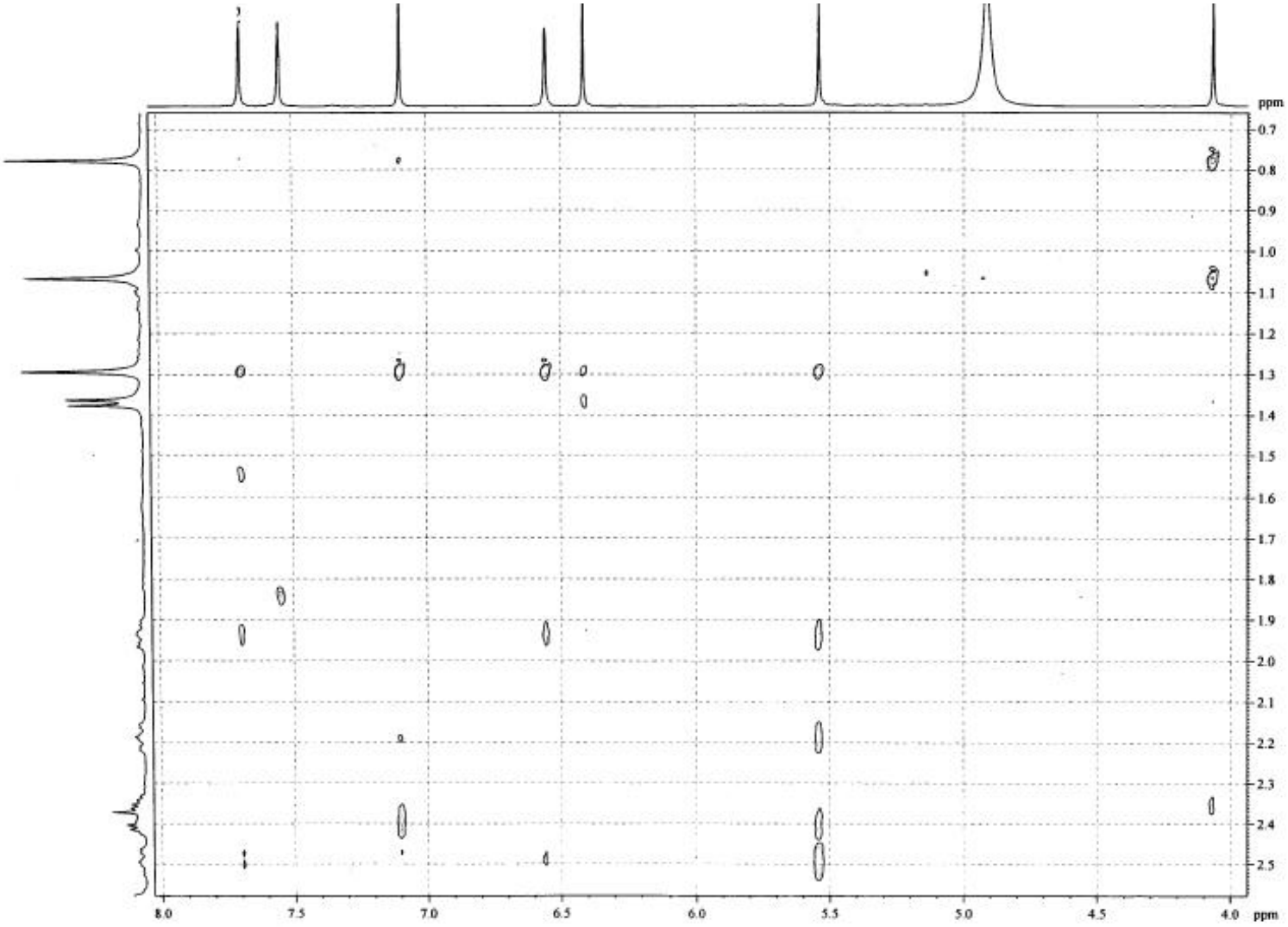
A Segment of NOESY Spectrum of xylogranatin I (**4**) in methanol-d_4



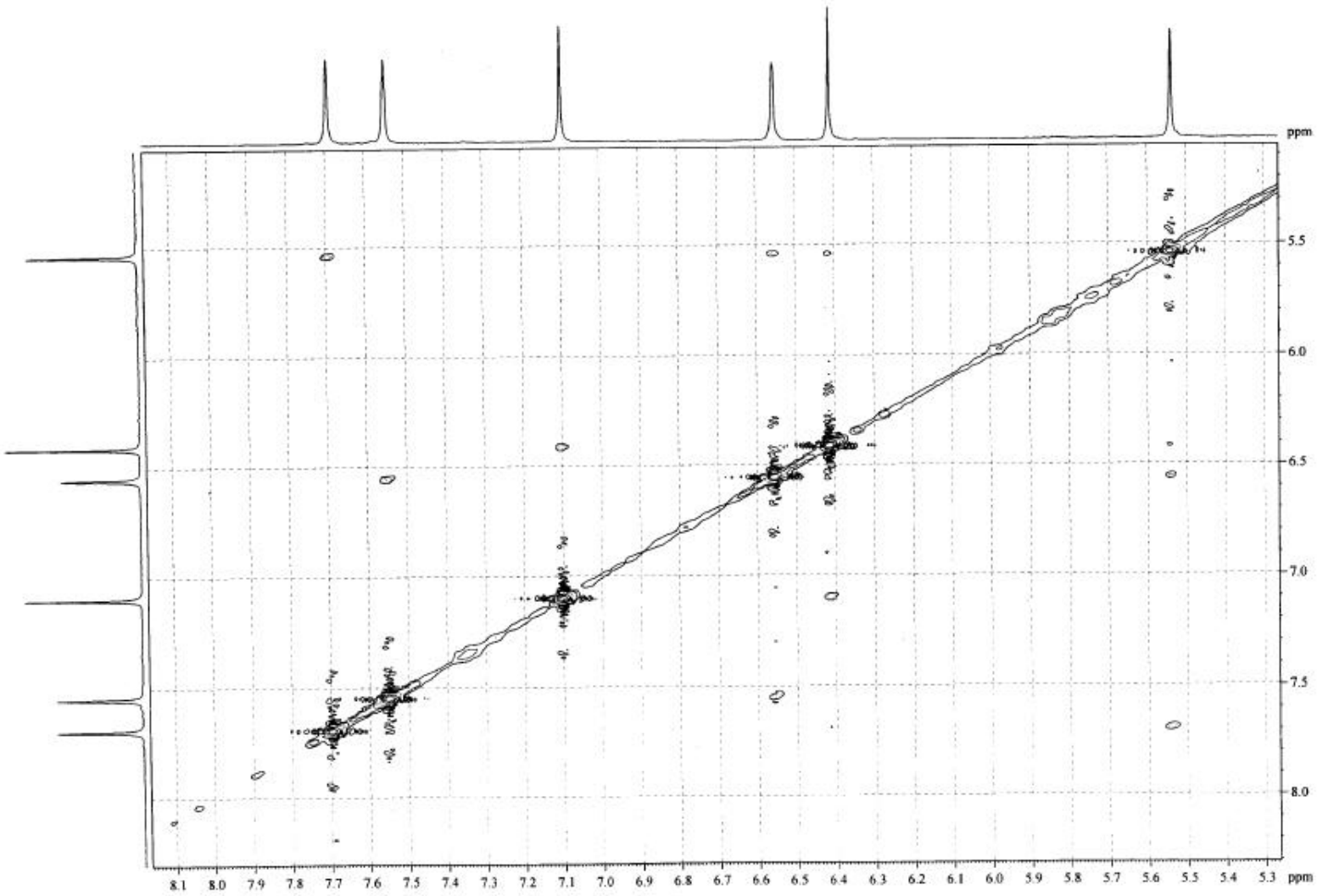
A Segment of NOESY Spectrum of xylogranatin I (**4**) in methanol-d_4



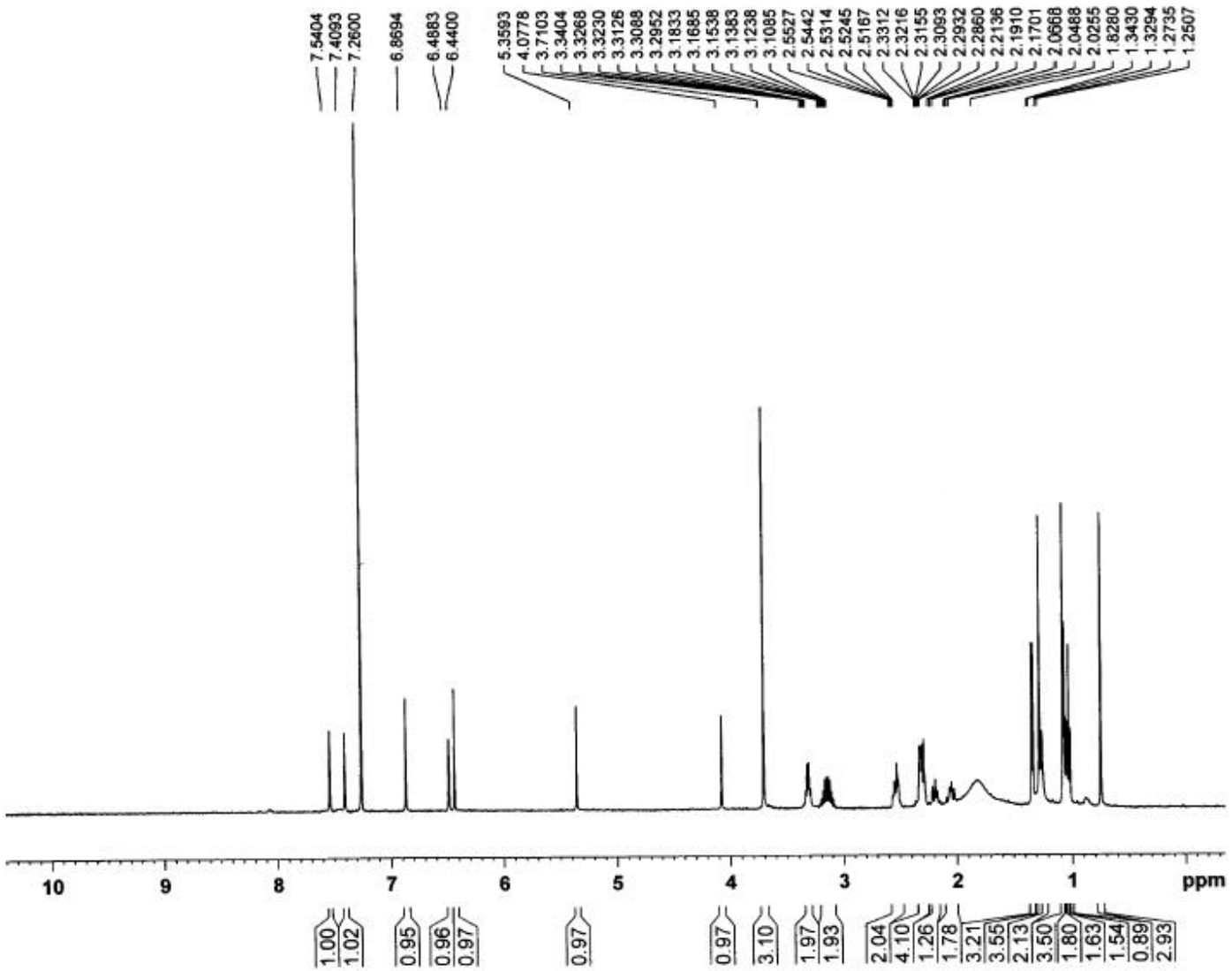
A Segment of NOESY Spectrum of xylogranatin I (**4**) in methanol-d_4



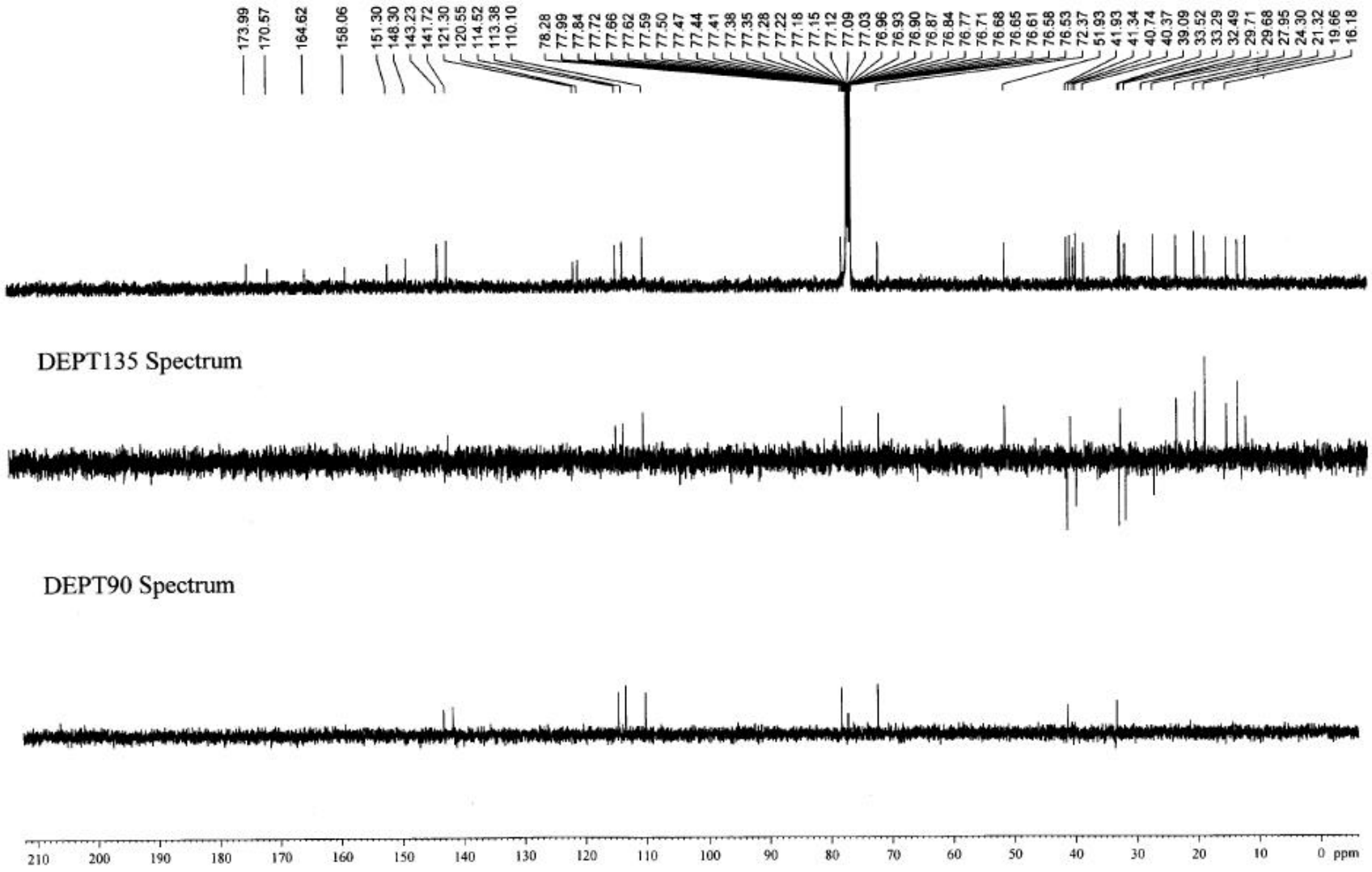
A Segment of NOESY Spectrum of xylogranatin I (**4**) in methanol-d_4



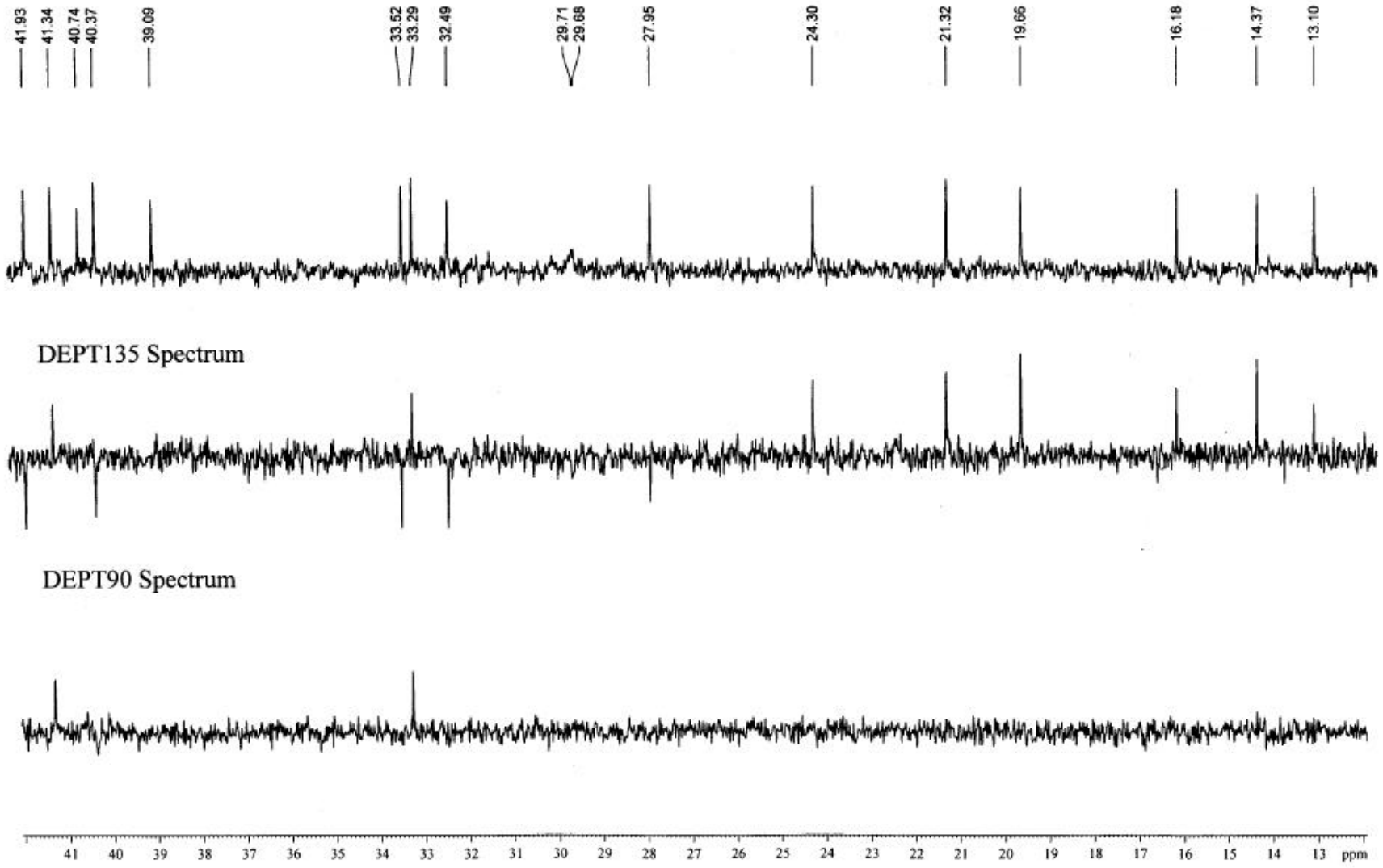
^{1}H NMR (500 MHz) Spectrum of **4¢** in $CDCl_3$



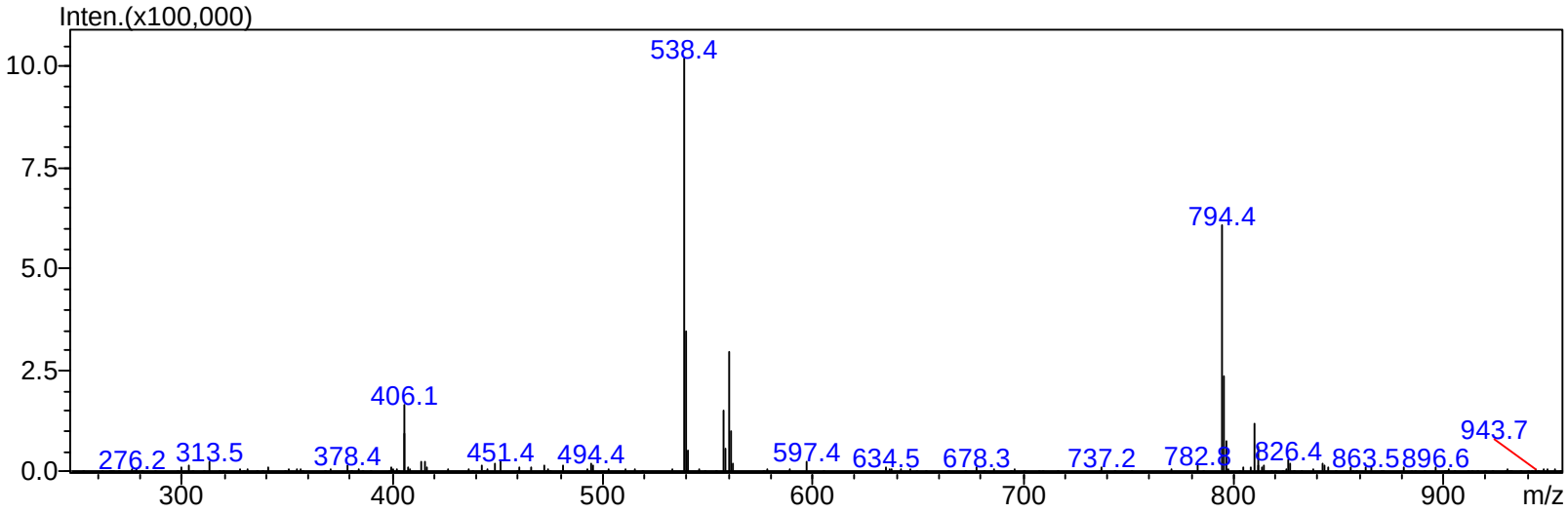
^{13}C NMR (125 MHz) Spectrum and DEPT experiments of **4¢** in $CDCl_3$



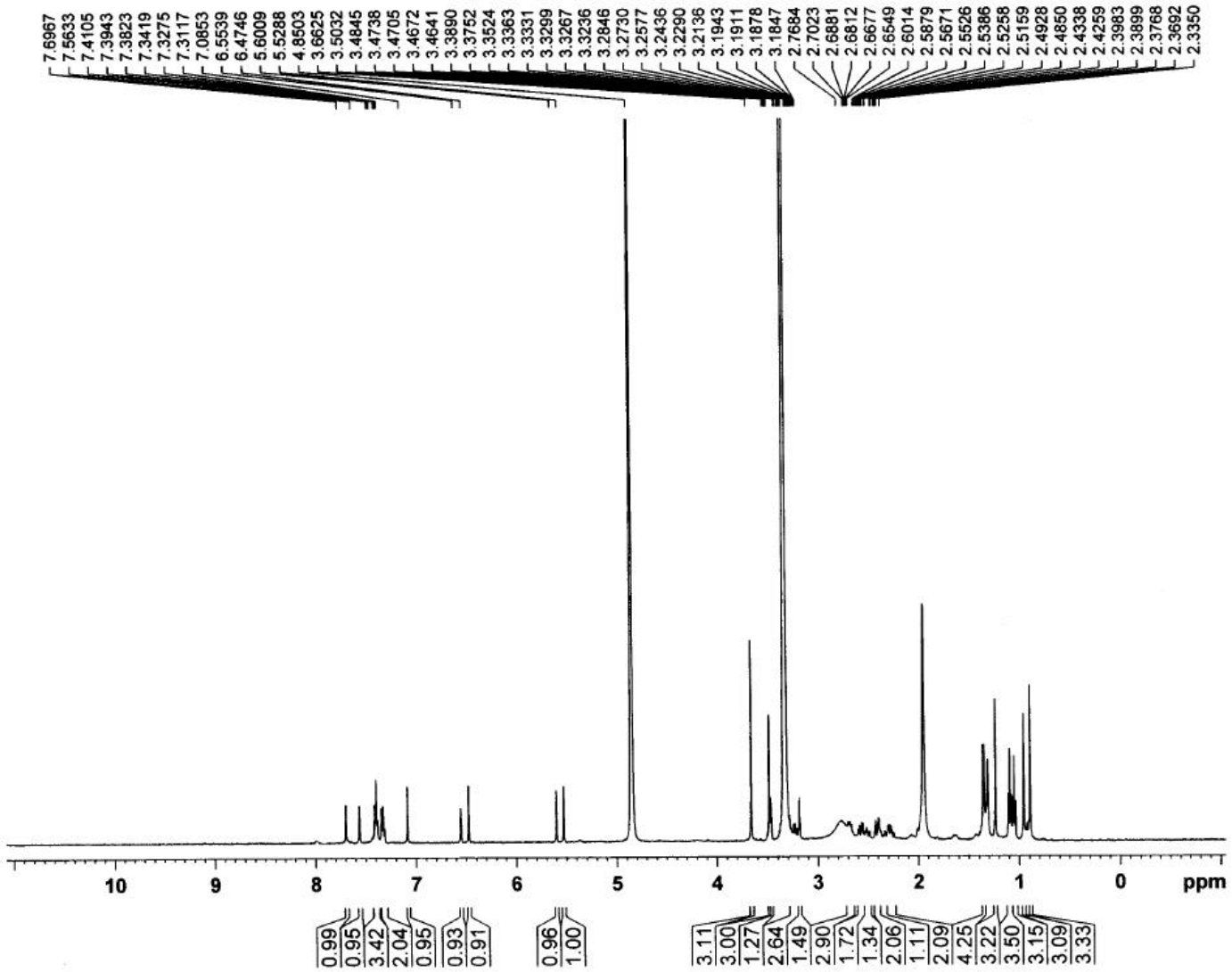
A Segment of ^{13}C NMR (125 MHz) Spectrum and DEPT experiments of **4¢** in $CDCl_3$



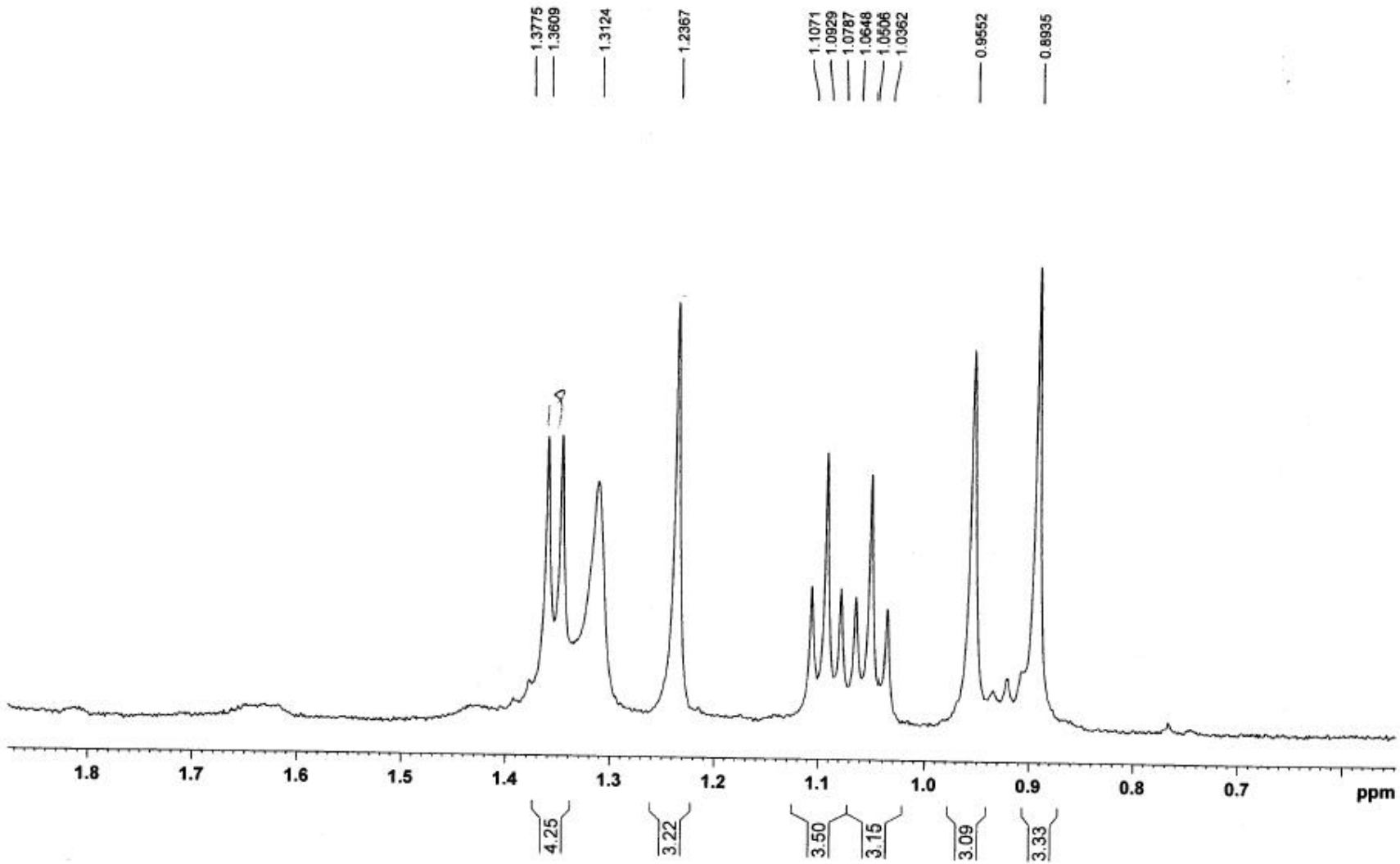
ESI-MS of **4¢s**


Inten.(x100,000)
10.0
7.5
5.0
2.5
0.0
538.4
794.4
406.1
943.7
276.2
313.5
378.4
451.4
494.4
597.4
634.5
678.3
737.2
782.8
826.4
863.5
896.6
300
400
500
600
700
800
900
m/z

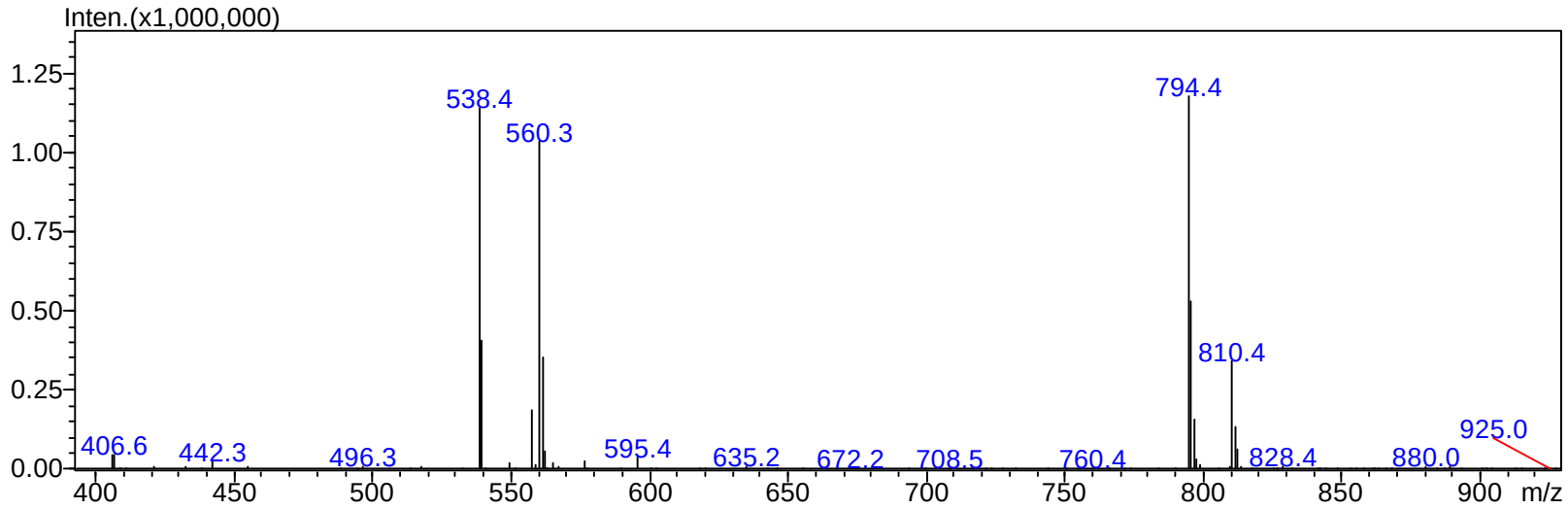
^{1}H NMR (500 MHz) of **4¢s** in methanol-d_4



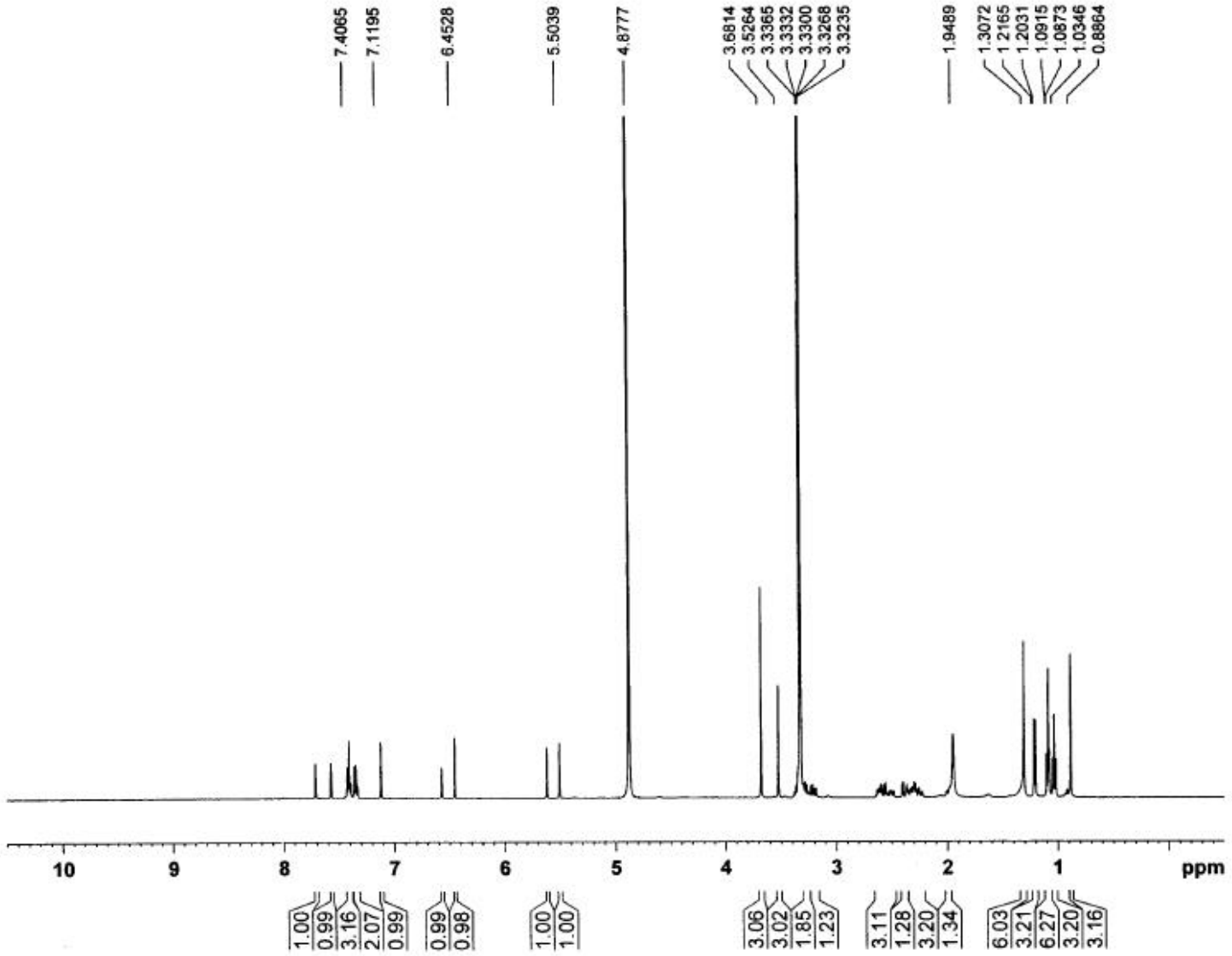
A Segment of ^{1}H NMR (500 MHz) of **4¢s** in methanol-d_4



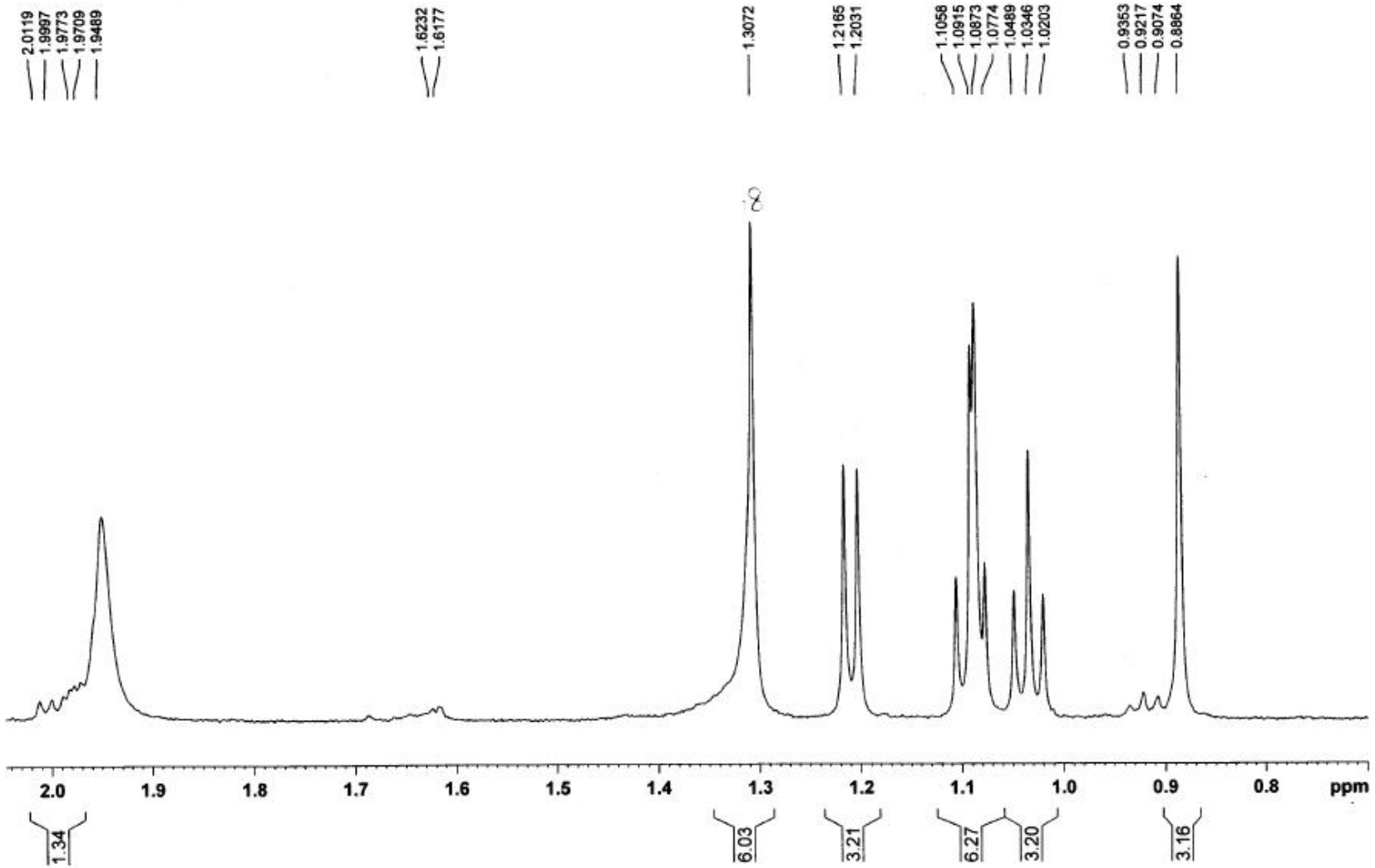
ESI-MS of **4¢r**


Inten.(x1,000,000)
1.25
1.00
0.75
0.50
0.25
0.00
538.4
560.3
794.4
810.4
406.6
442.3
496.3
595.4
635.2
672.2
708.5
760.4
828.4
880.0
925.0
400
450
500
550
600
650
700
750
800
850
900
m/z

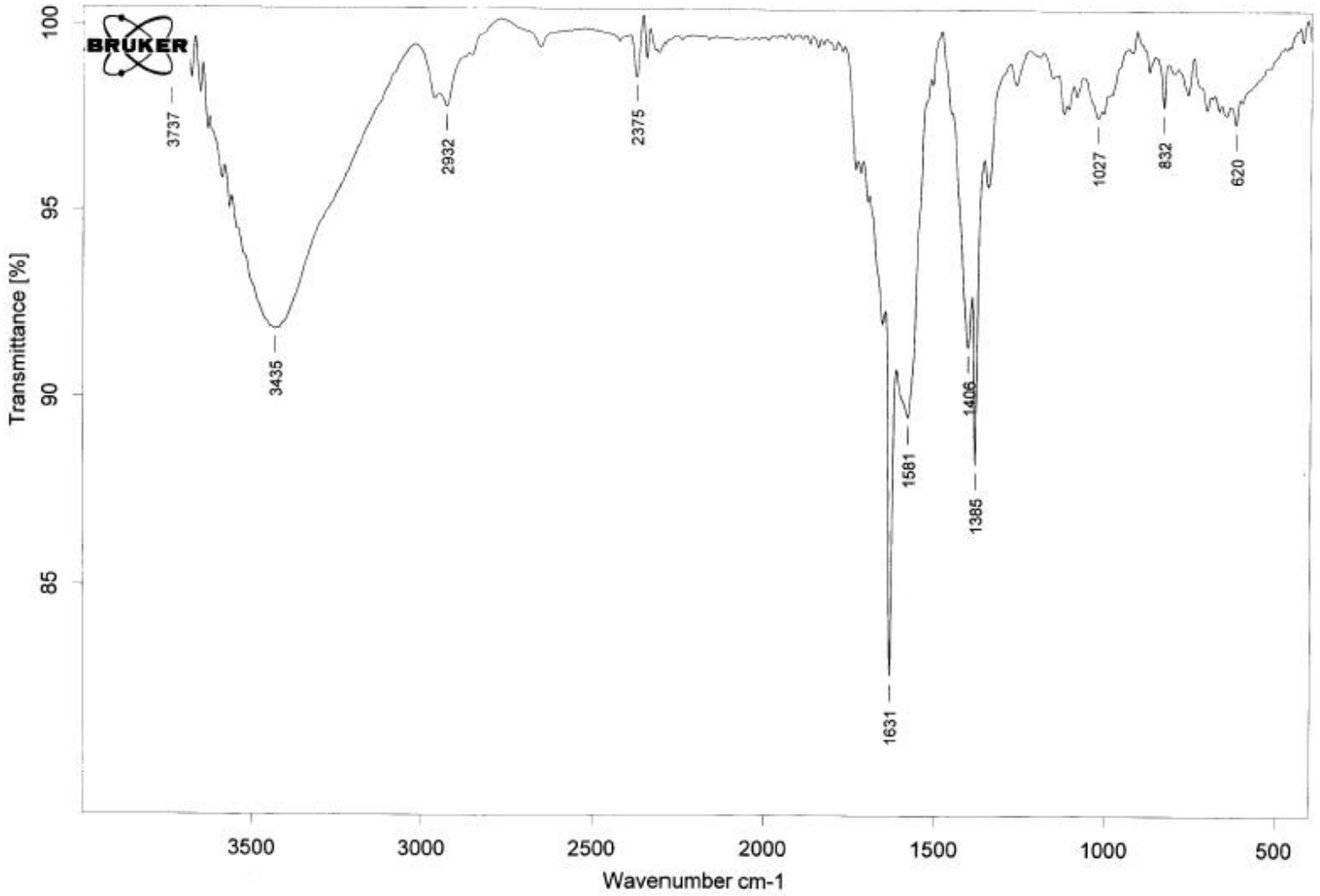
^{1}H NMR (500 MHz) of **4¢r** in methanol-d_4



A Segment of ^{1}H NMR (500 MHz) of **4¢r** in methanol-d_4



IR spectrum of xylogranatin J (**5**)



HR-TOFMS of xylogranatin J (**5**)

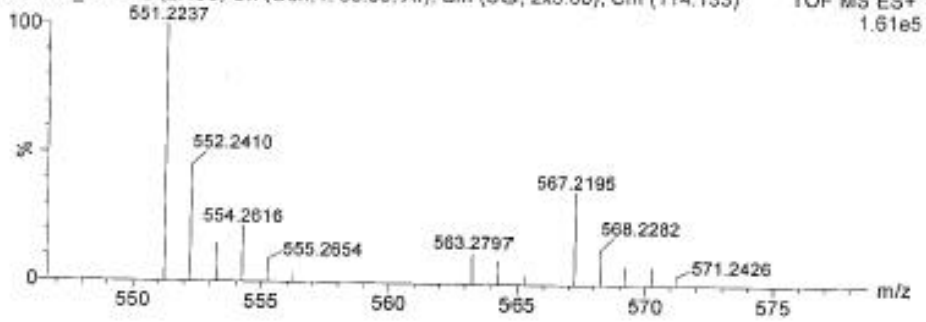
Elemental Composition Report

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

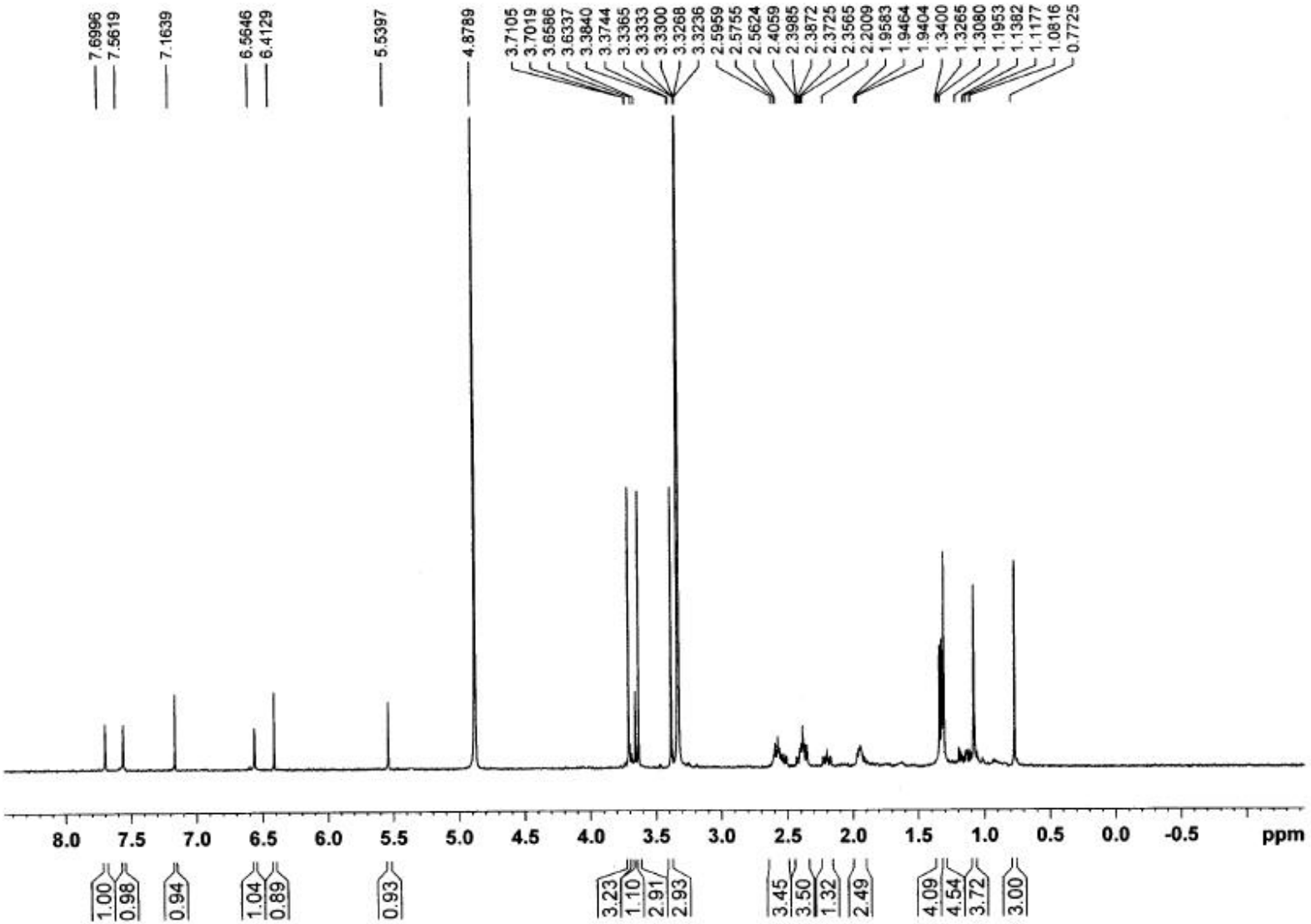
Monoisotopic Mass, Odd and Even Electron Ions
55 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

Minimum:				-1.5		
Maximum:		200.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
551.2237	551.2257	-2.0	-3.6	11.5	2	C29 H36 O9 23Na
	551.2281	-4.4	-8.0	14.5	1	C31 H35 O9

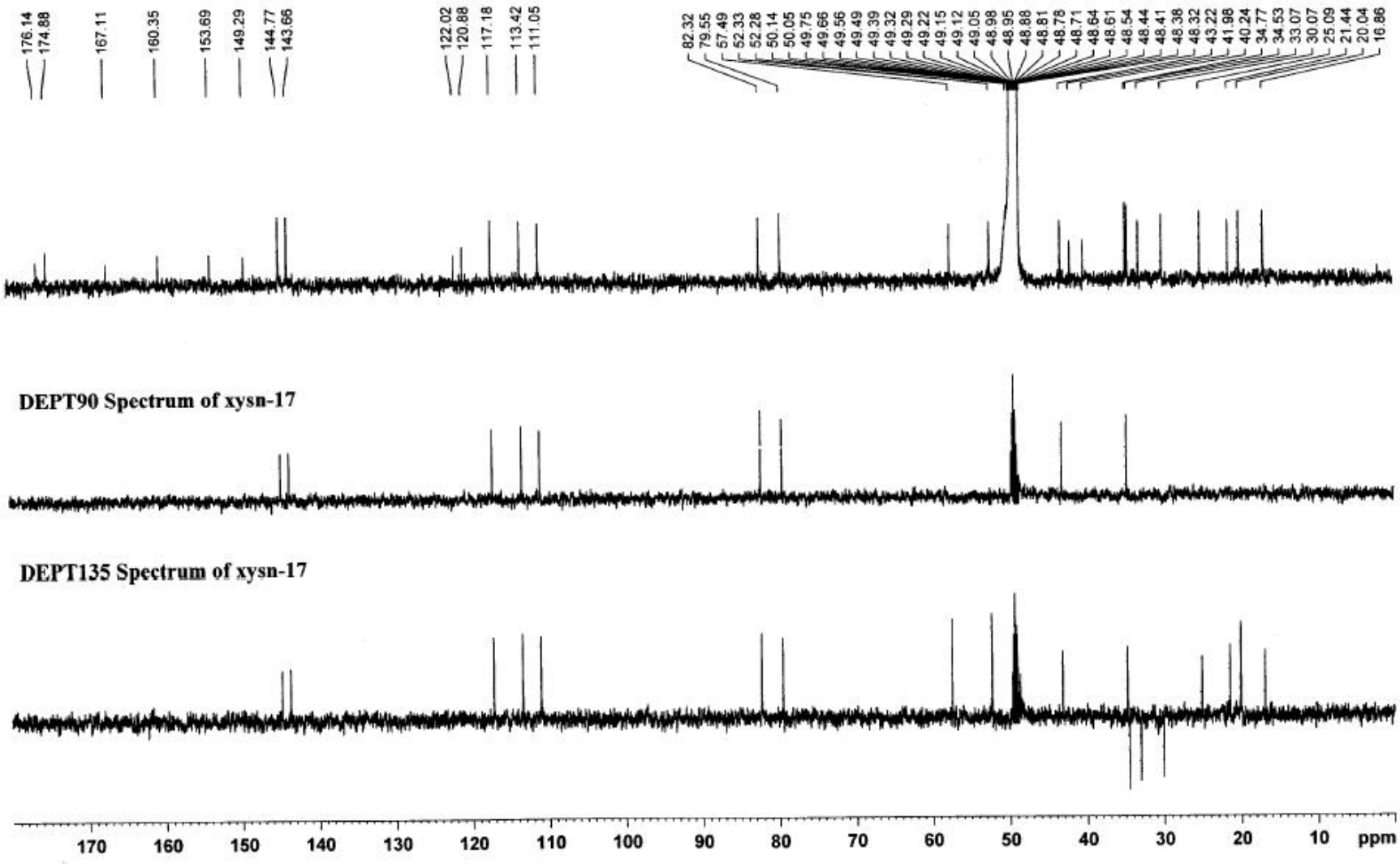
Wu05
060929_08 115 (2.198) Cn (Cen,4, 80.00, Ar); Sm (SG, 2x3.00); Cm (114:133) TOF MS ES+
1.61e5



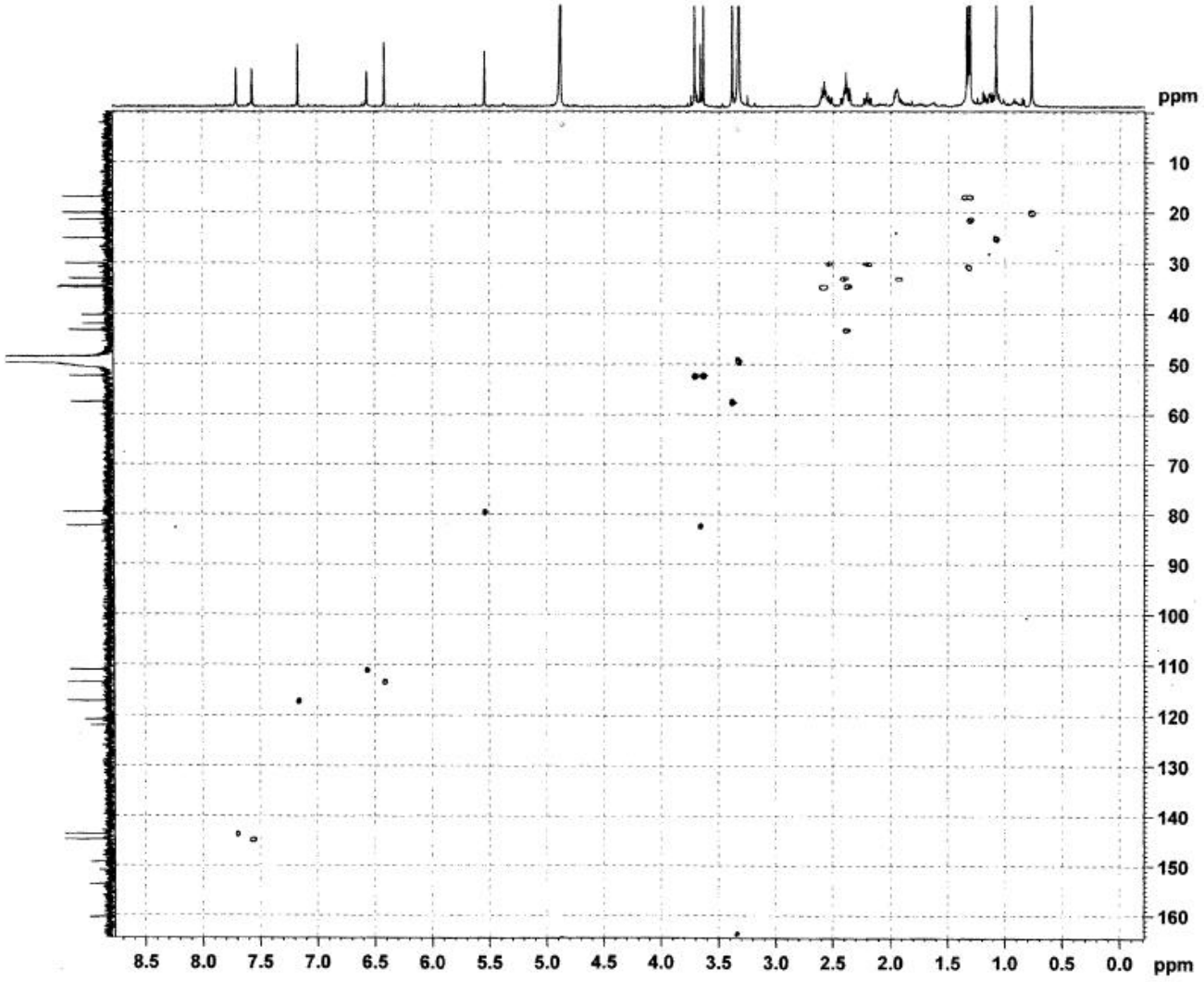
^{1}H NMR (500 MHz) Spectrum of xylogranatin J (**5**) in methanol-d_4



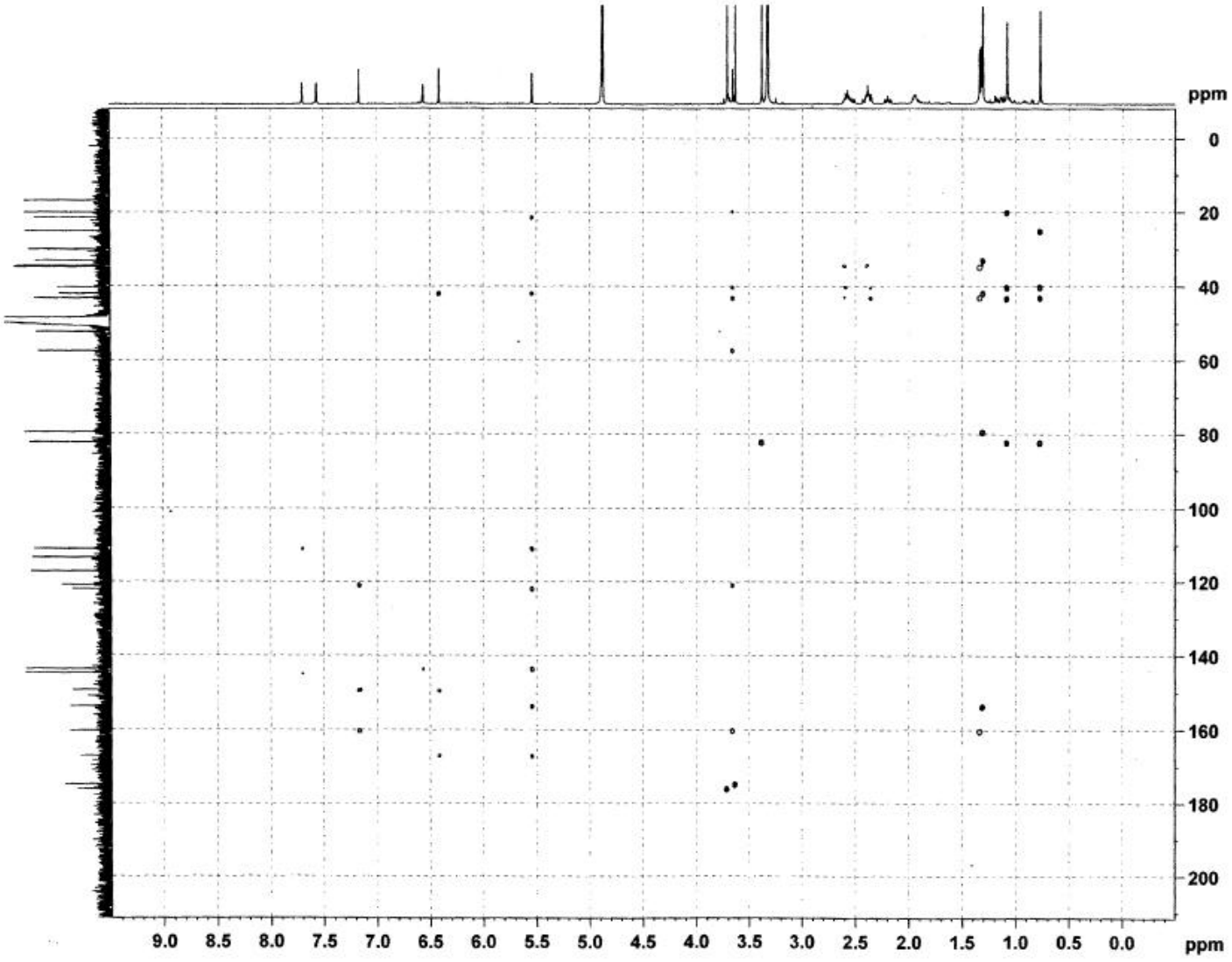
^{13}C NMR (125 MHz) Spectrum and DEPT experiments of xylogranatin J (**5**) in methanol-d_4



HSQC Spectrum of xylogranatin J (**5**) in methanol-d_4

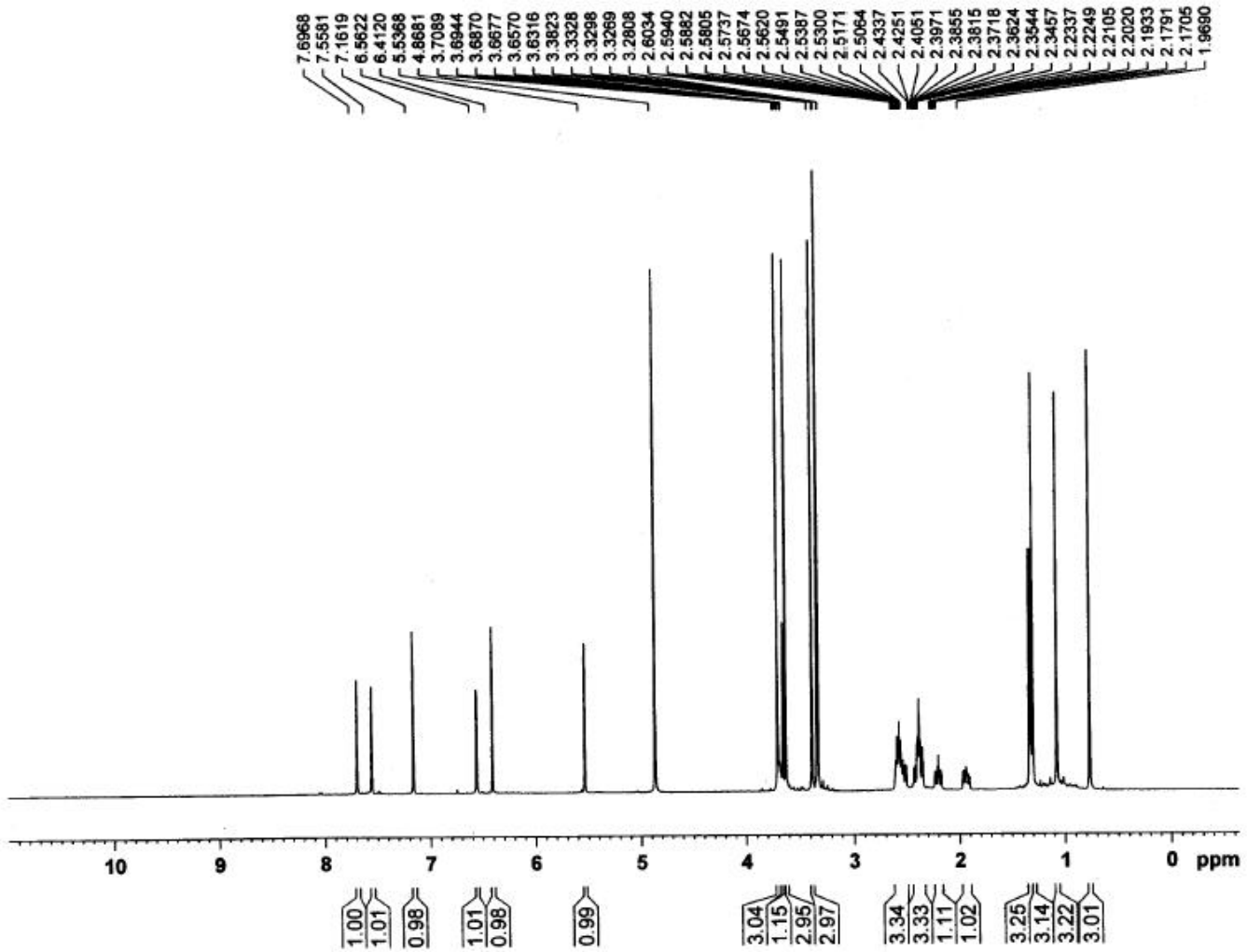


HMBC Spectrum of xylogranatin J (**5**) in methanol-d_4

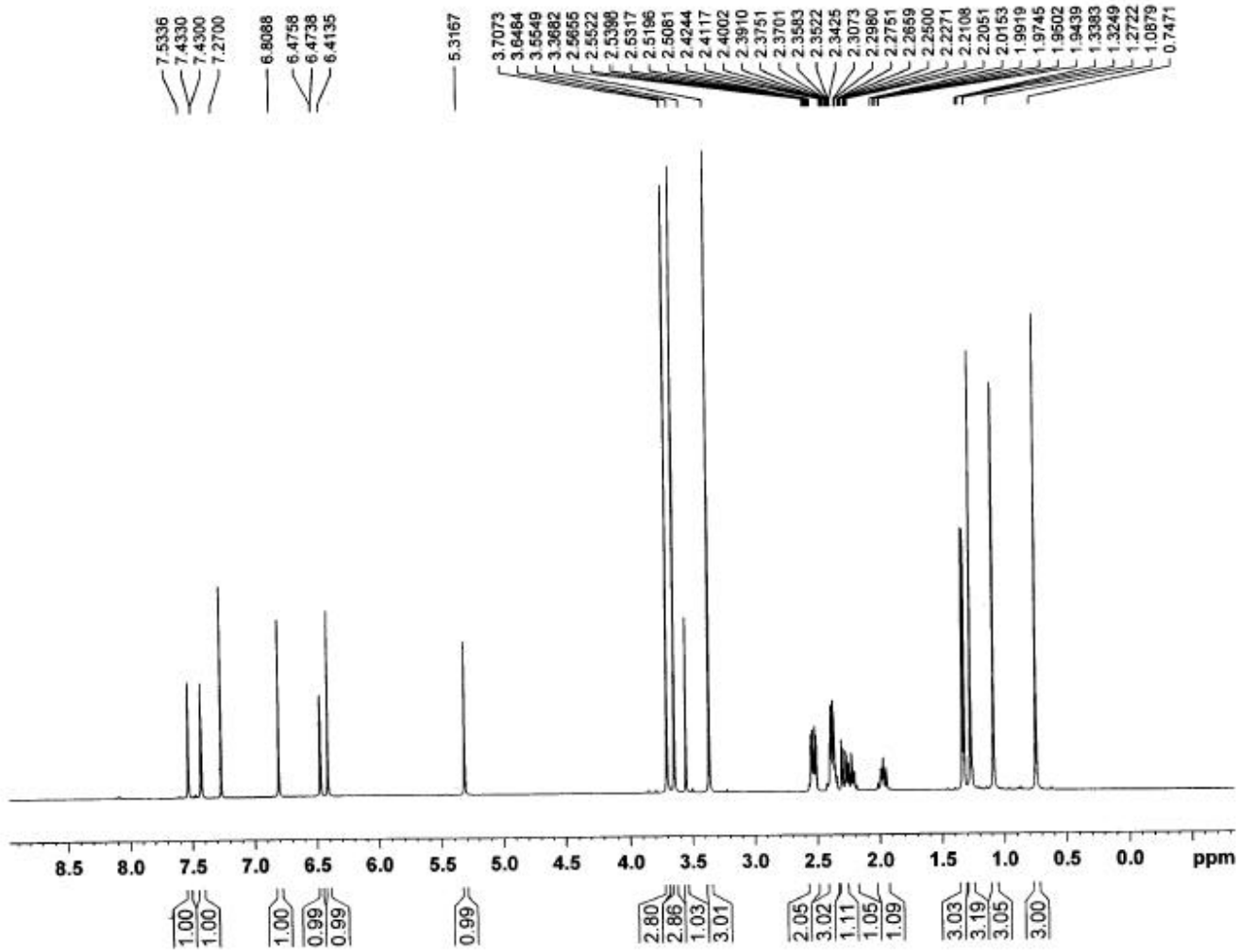


^{1}H NMR (500 MHz) Spectrum of the Major Product **(5)** Detected in methanol-d_4

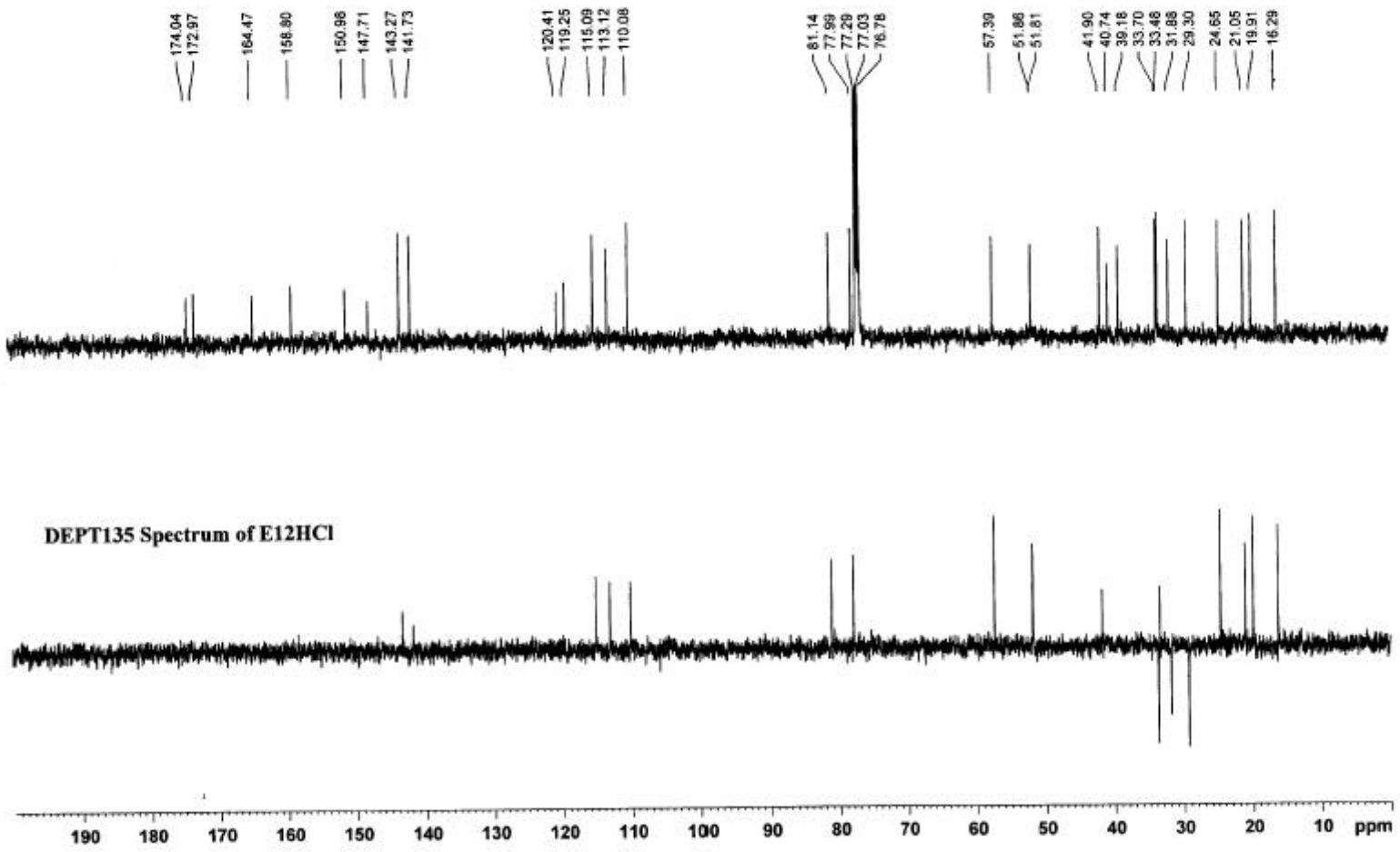
(Treatment of **4** with 30% hydrochloric acid in methanol)



^{1}H NMR (500 MHz) Spectrum of the Major Product **(5)** Detected in $CDCl_3$
(Treatment of **4** with 30% hydrochloric acid in methanol)

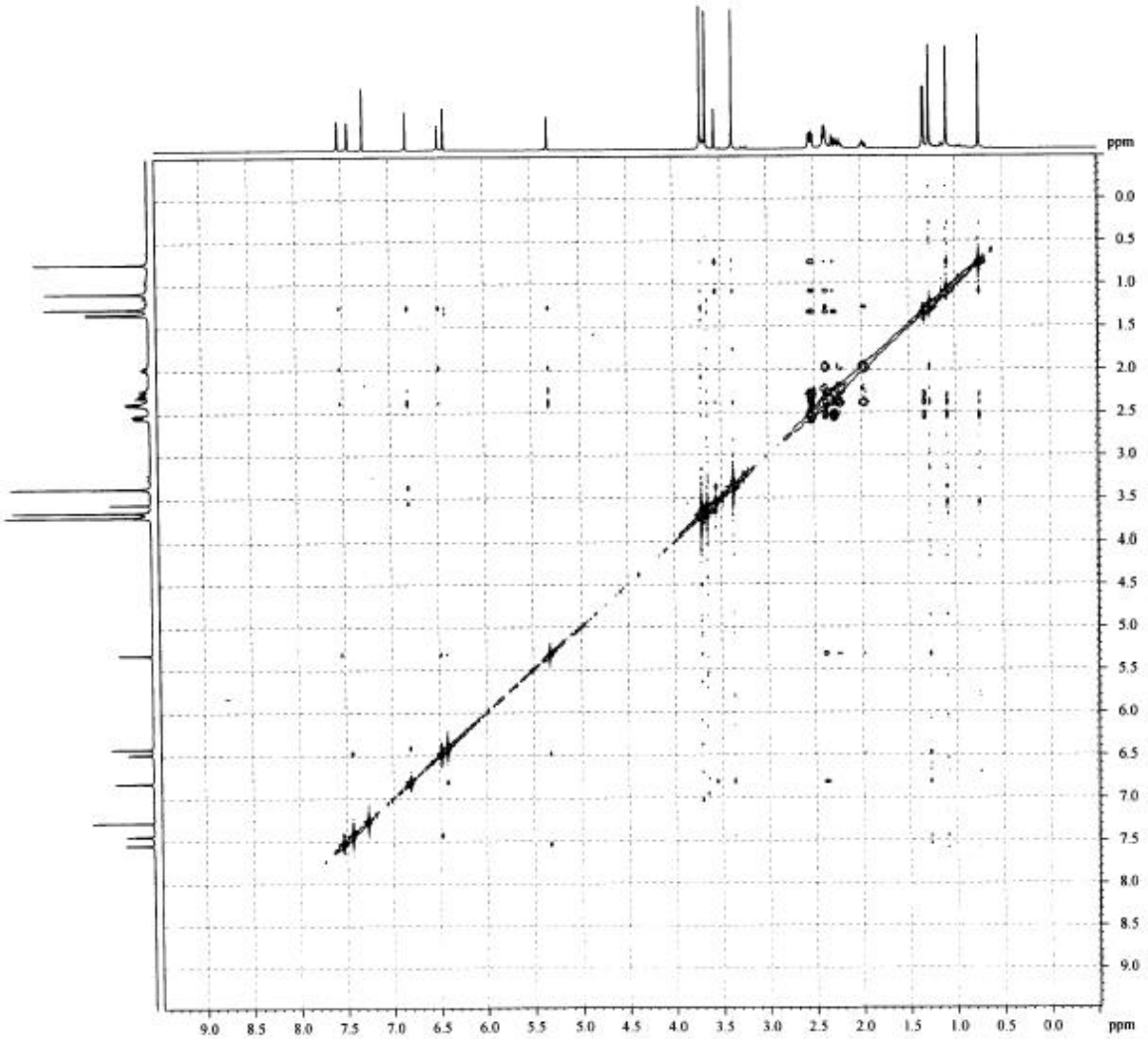


^{13}C NMR (125 MHz) Spectrum and DEPT experiments of the Major Product **(5)** Detected in $CDCl_3$ (Treatment of **4** with 30% hydrochloric acid in methanol)



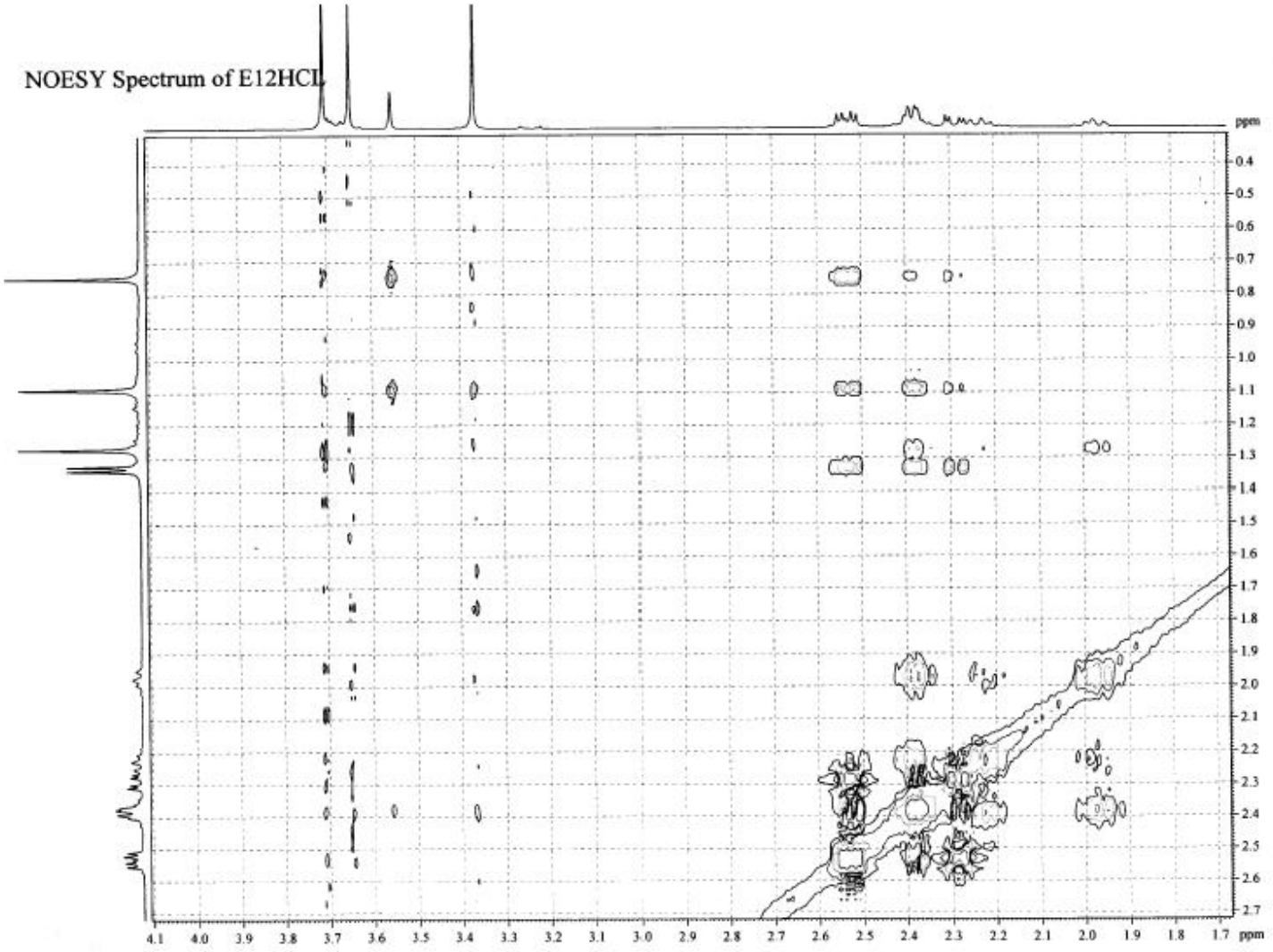
NOESY Spectrum of the Major Product **(5)** Detected in $CDCl_3$

(Treatment of **4** with 30% hydrochloric acid in methanol)



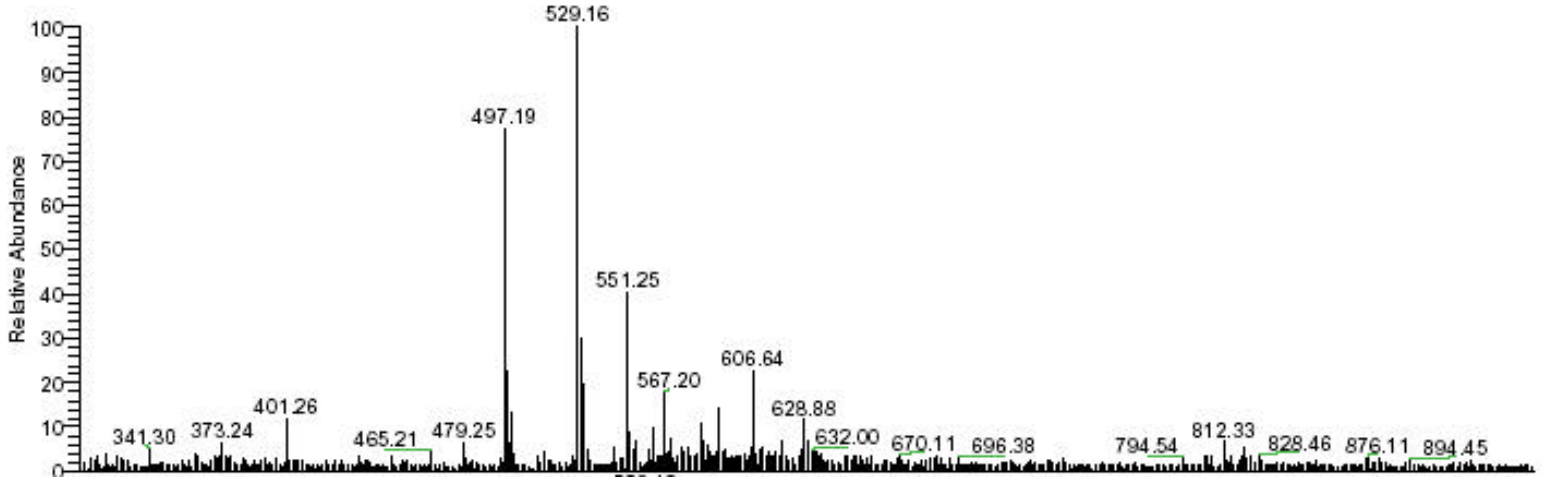
A Segment of NOESY Spectrum of the Major Product **(5)** Detected in $CDCl_3$

(Treatment of **4** with 30% hydrochloric acid in methanol)



ESI-MS of the Minor Product **(5¢)**

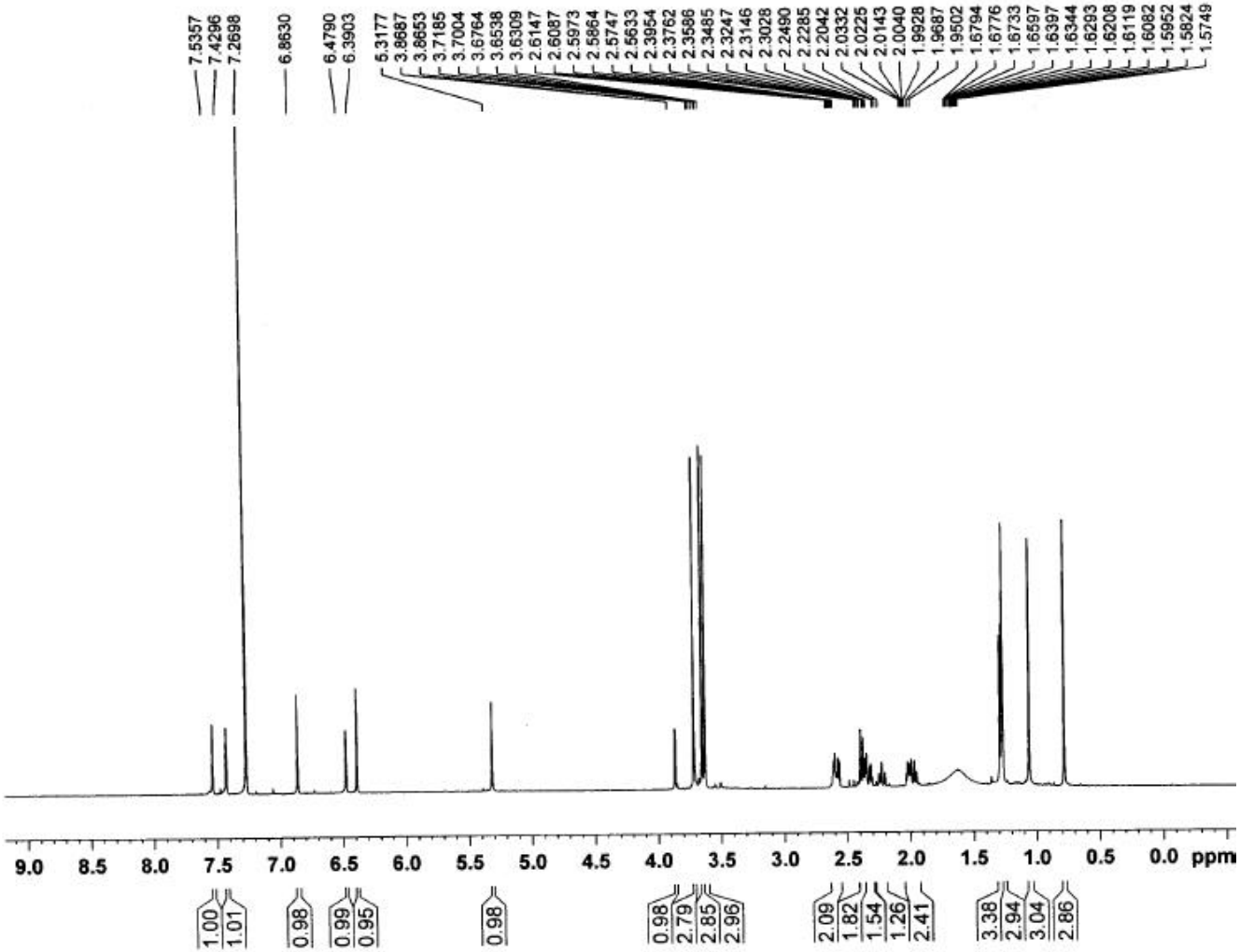
(Treatment of **4** with 30% hydrochloric acid in methanol)



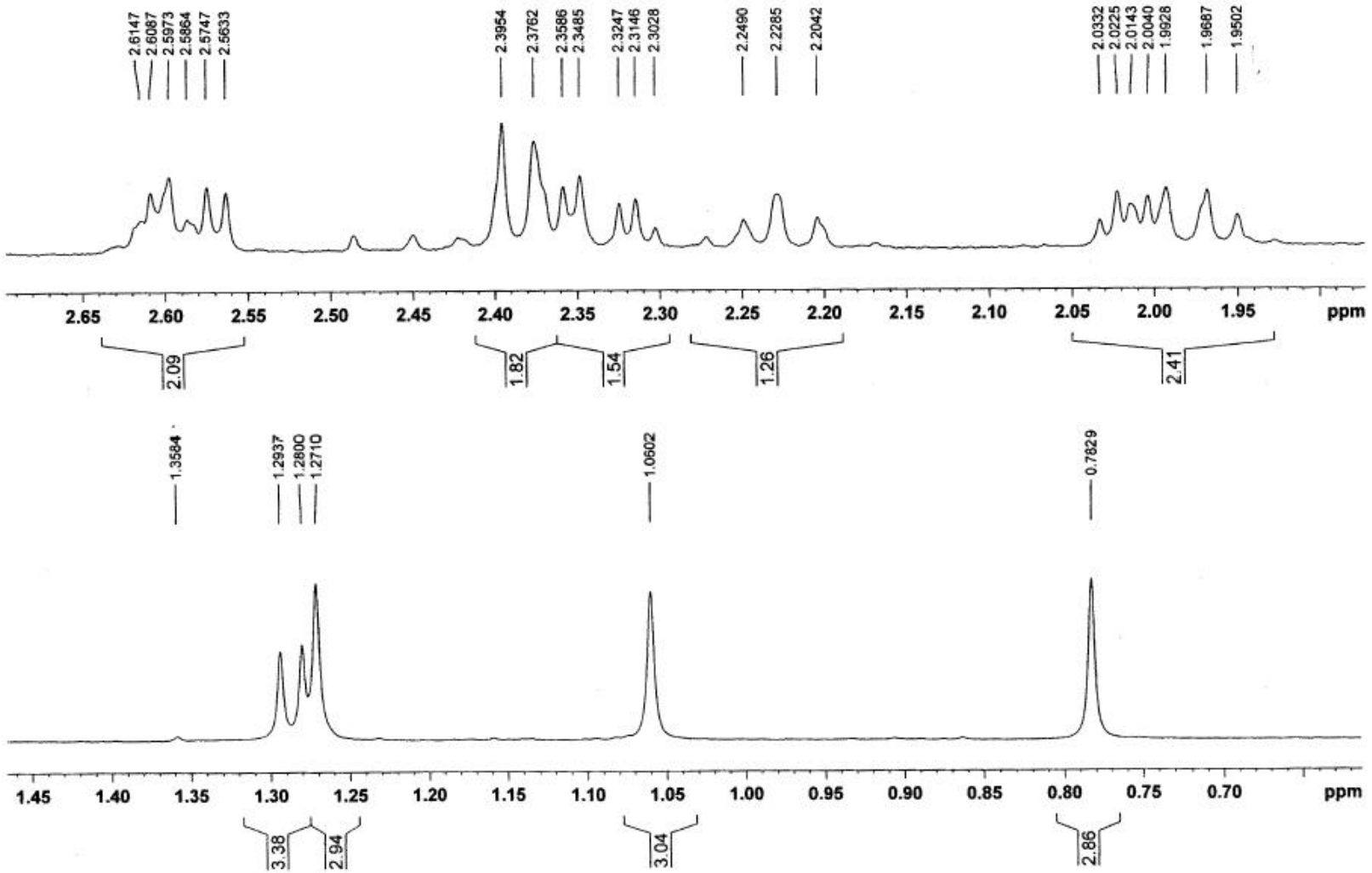
(Positive mode)

^{1}H NMR (500 MHz) Spectrum of the Minor Product **(5¢)** Detected in $CDCl_3$

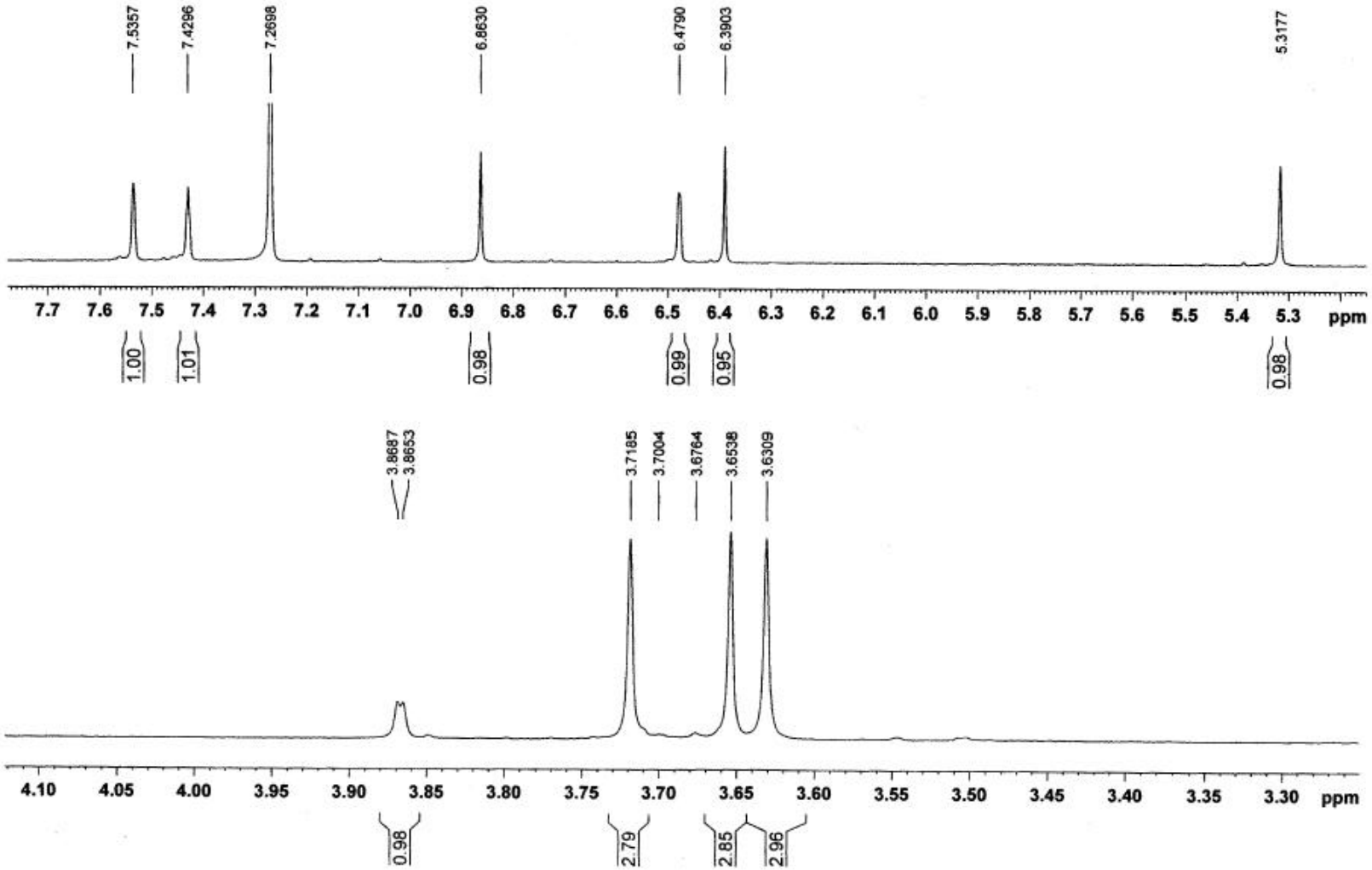
(Treatment of **4** with 30% hydrochloric acid in methanol)



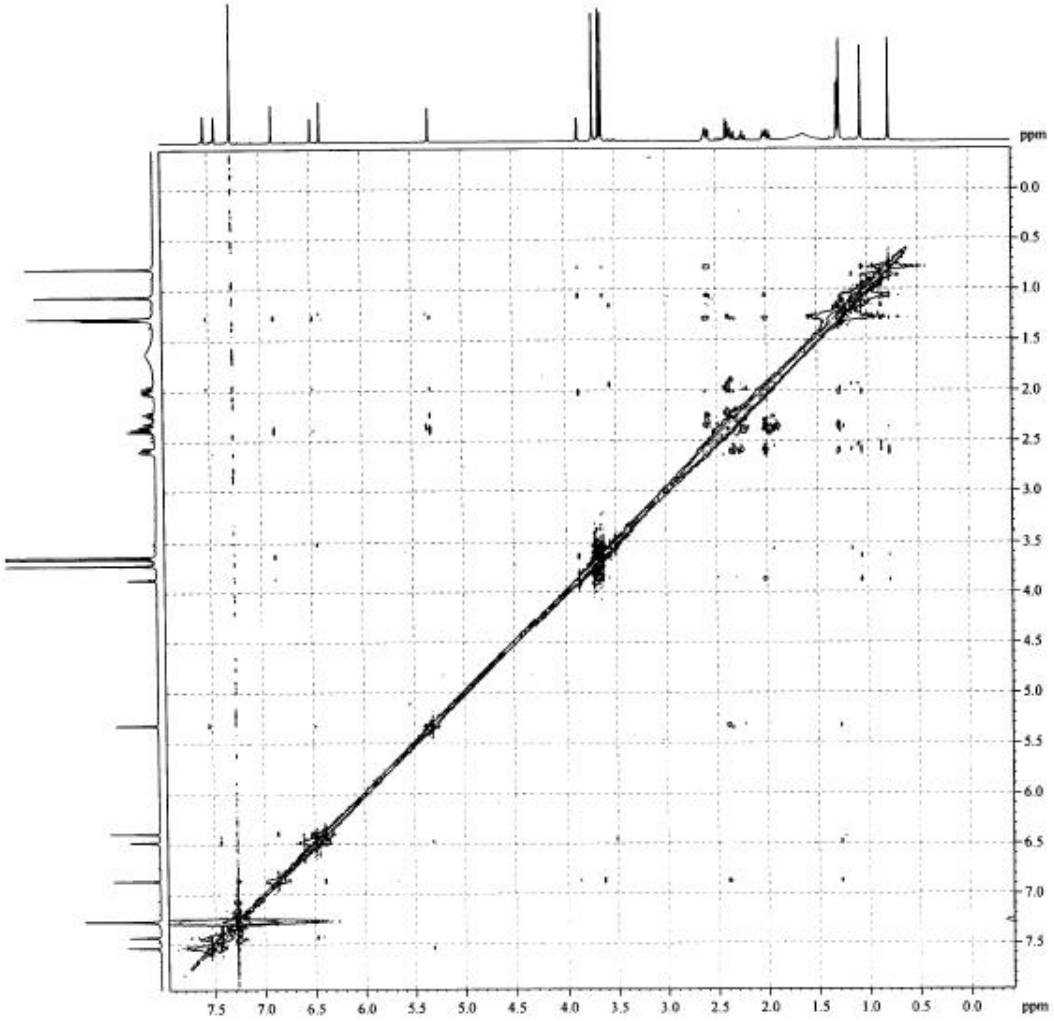
A Segment of ^{1}H NMR (500 MHz) Spectrum of **5¢** Detected in $CDCl_3$



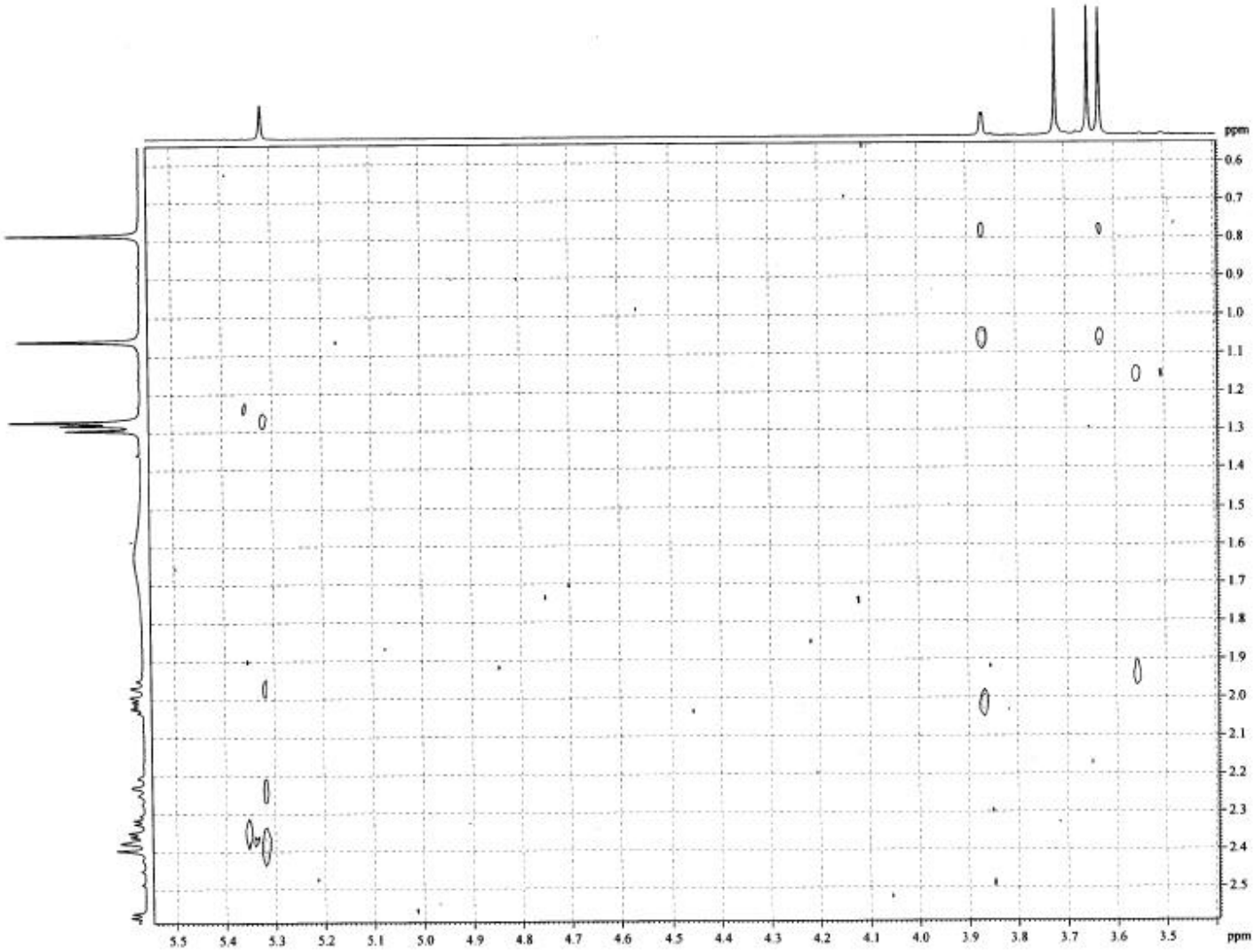
A Segment of ^{1}H NMR (500 MHz) Spectrum of **5¢** Detected in $CDCl_3$



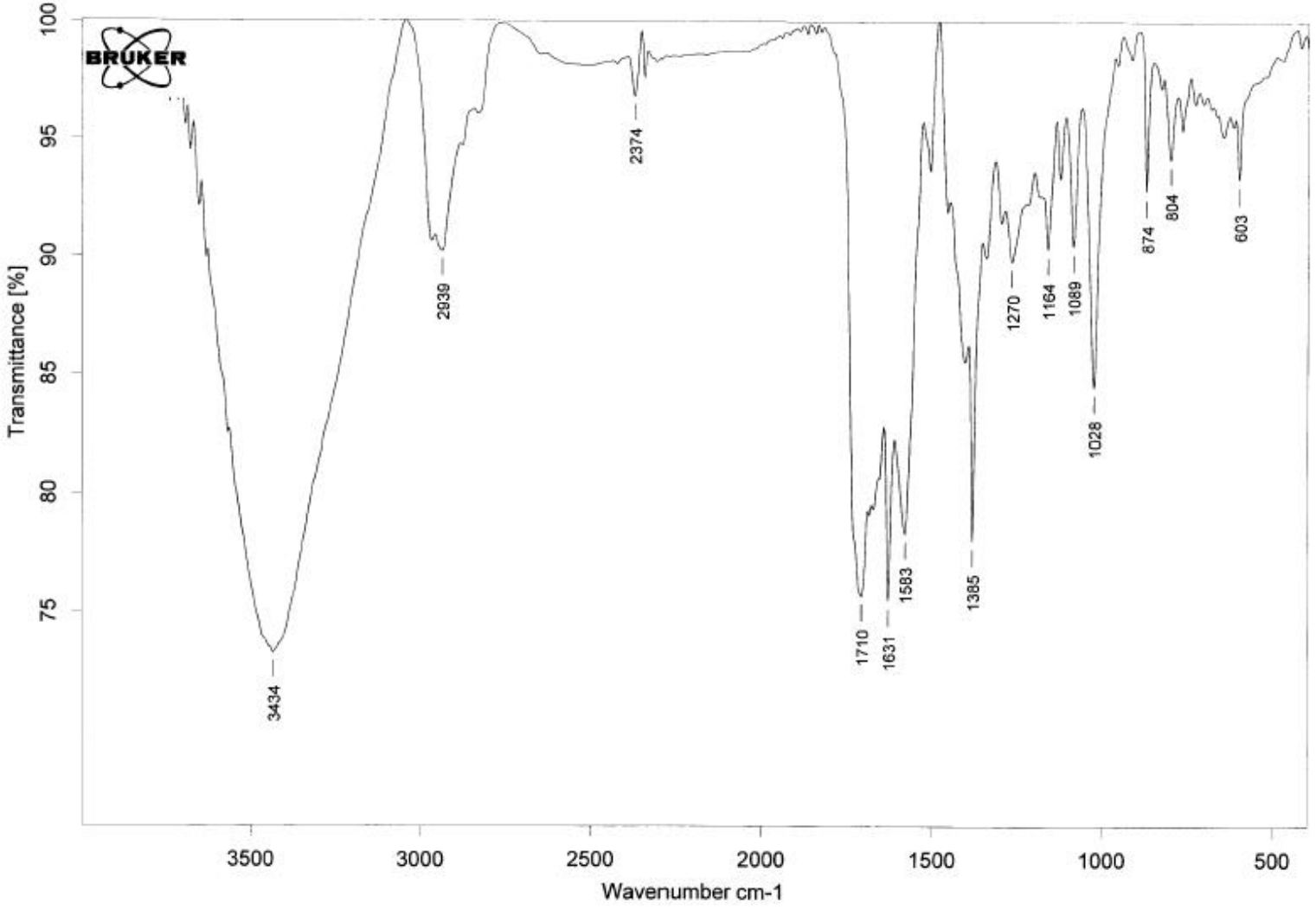
NOESY Spectrum of **5¢** Detected in $CDCl_3$



A Segment of NOESY Spectrum of **5¢** Detected in $CDCl_3$



IR spectrum of xylogranatin K (**6**)



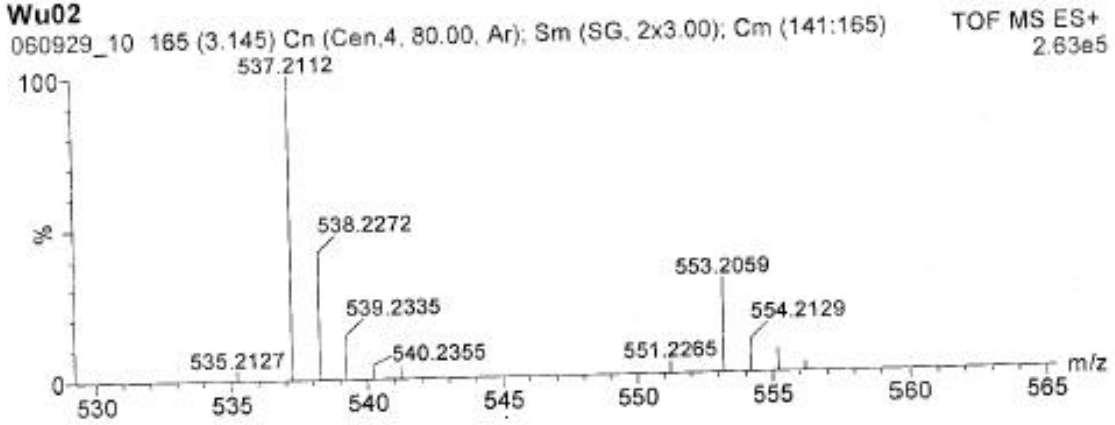
HR-TOFMS of xylogranatin K (**6**)

Elemental Composition Report

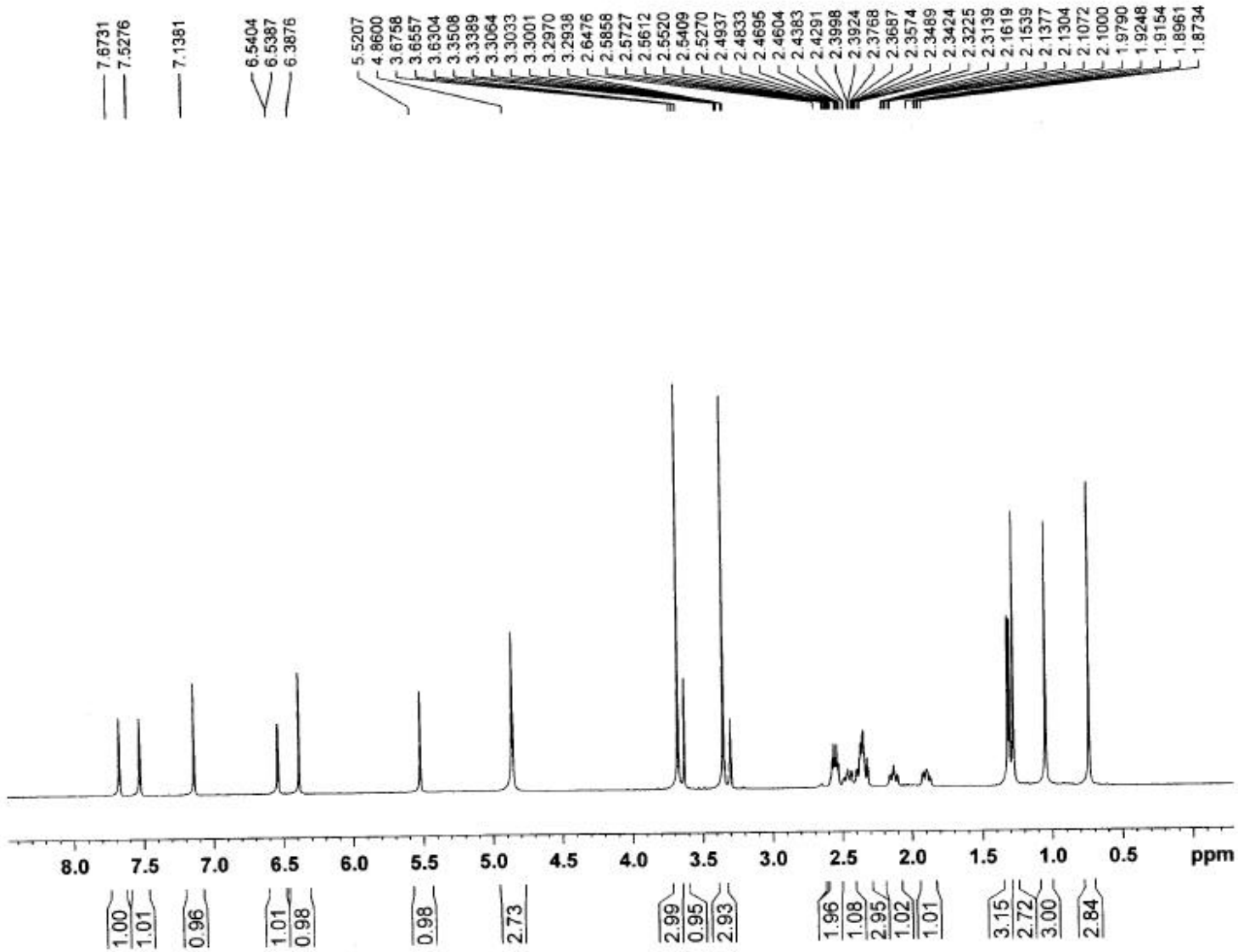
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
54 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

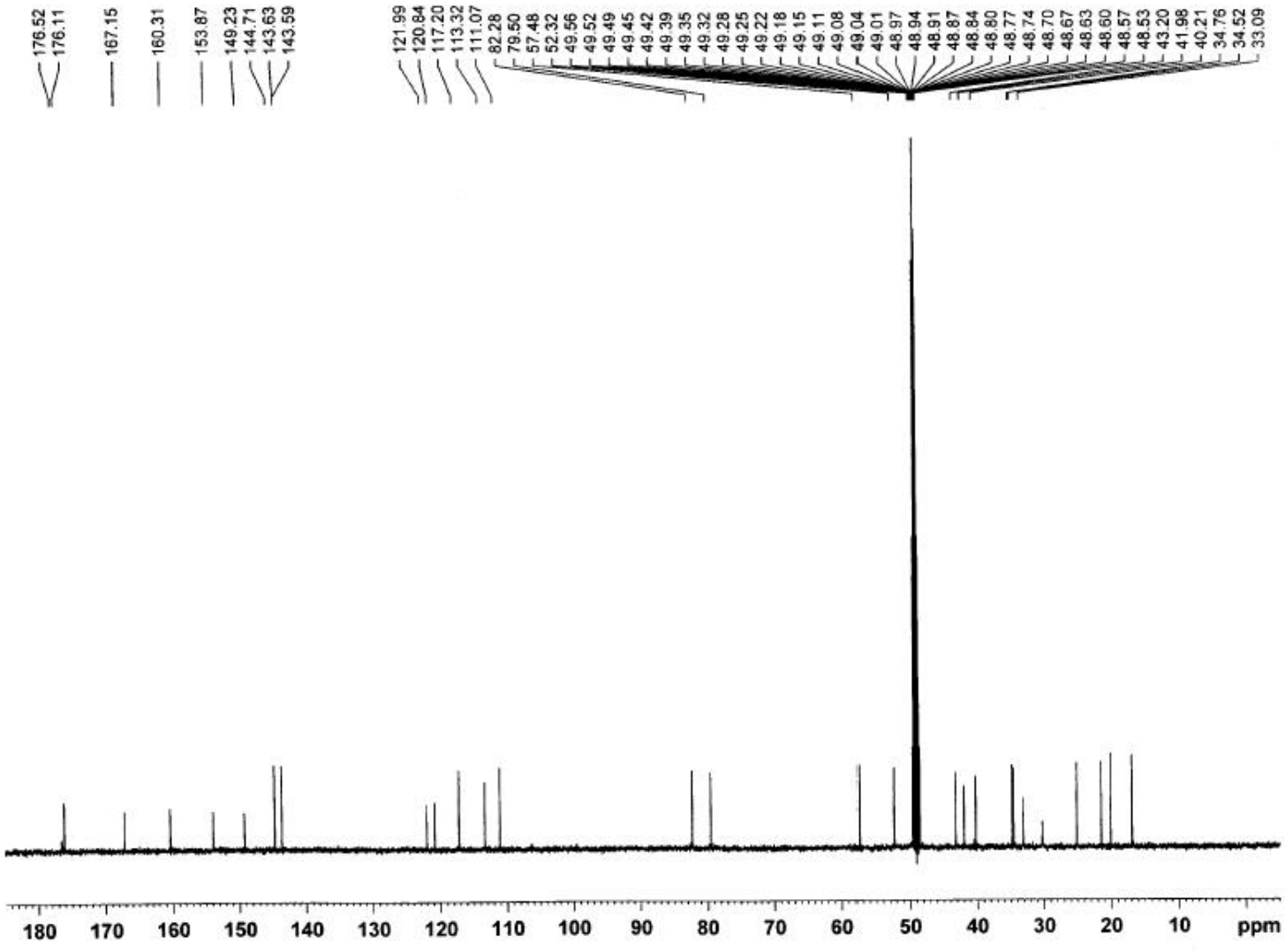
Minimum:				-1.5		
Maximum:		200.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
537.2112	537.2101	1.1	2.1	11.5	2	C28 H34 O9 23Na
	537.2125	-1.3	-2.3	14.5	1	C30 H33 O9



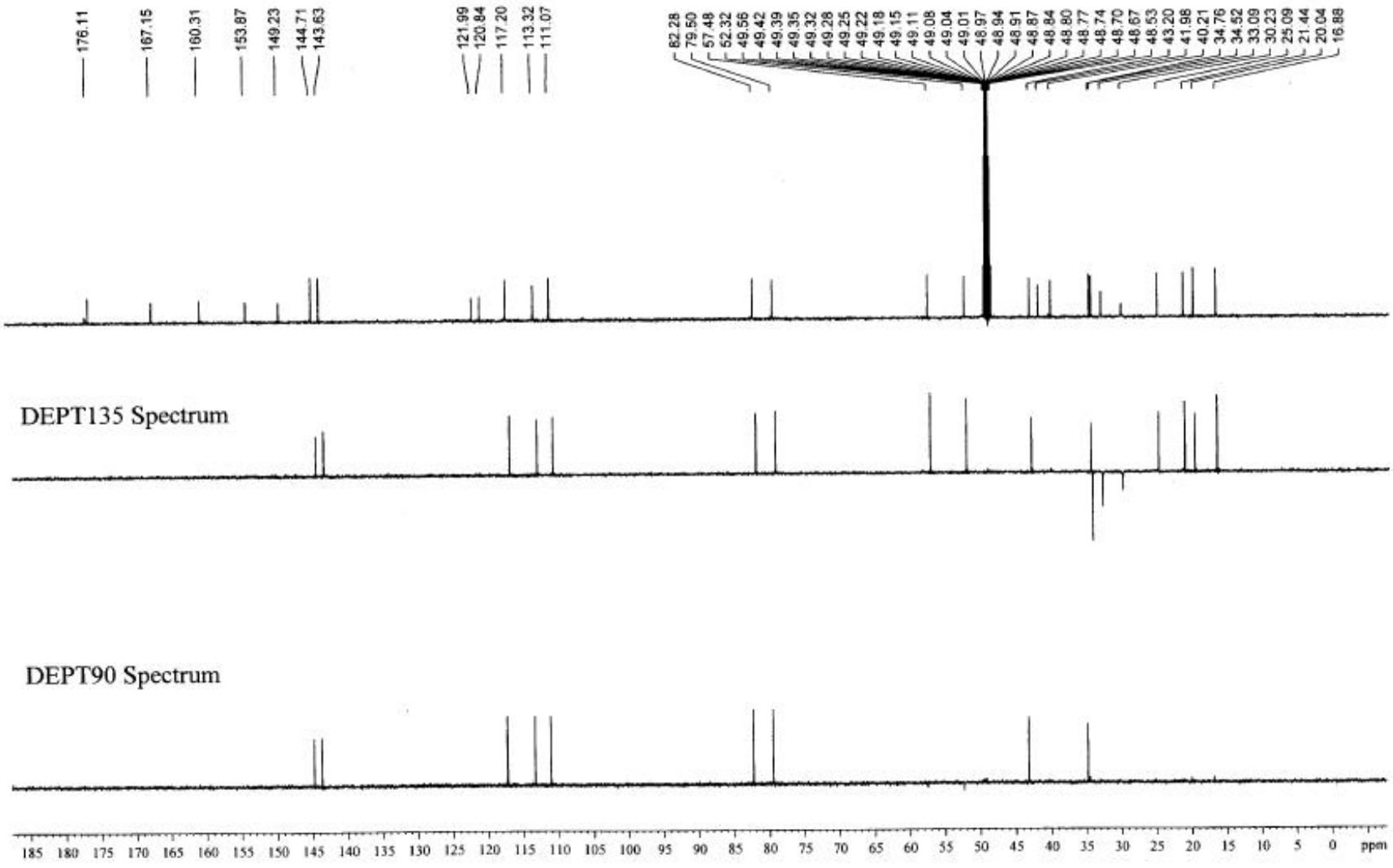
^{1}H NMR (500 MHz) Spectrum of xylogranatin K (**6**) in methanol-d_4



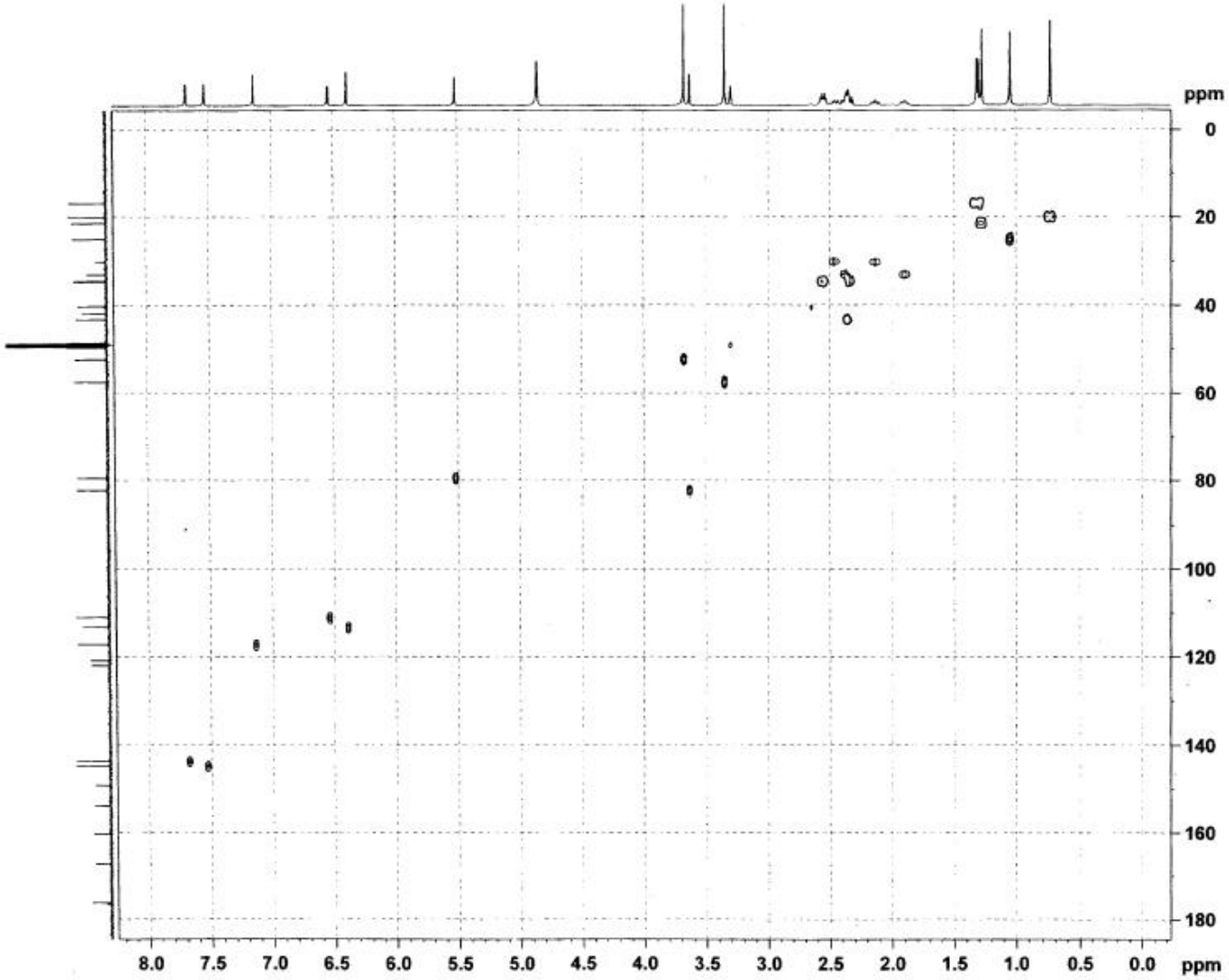
^{13}C NMR (125 MHz) Spectrum of xylogranatin K (**6**) in methanol-d_4



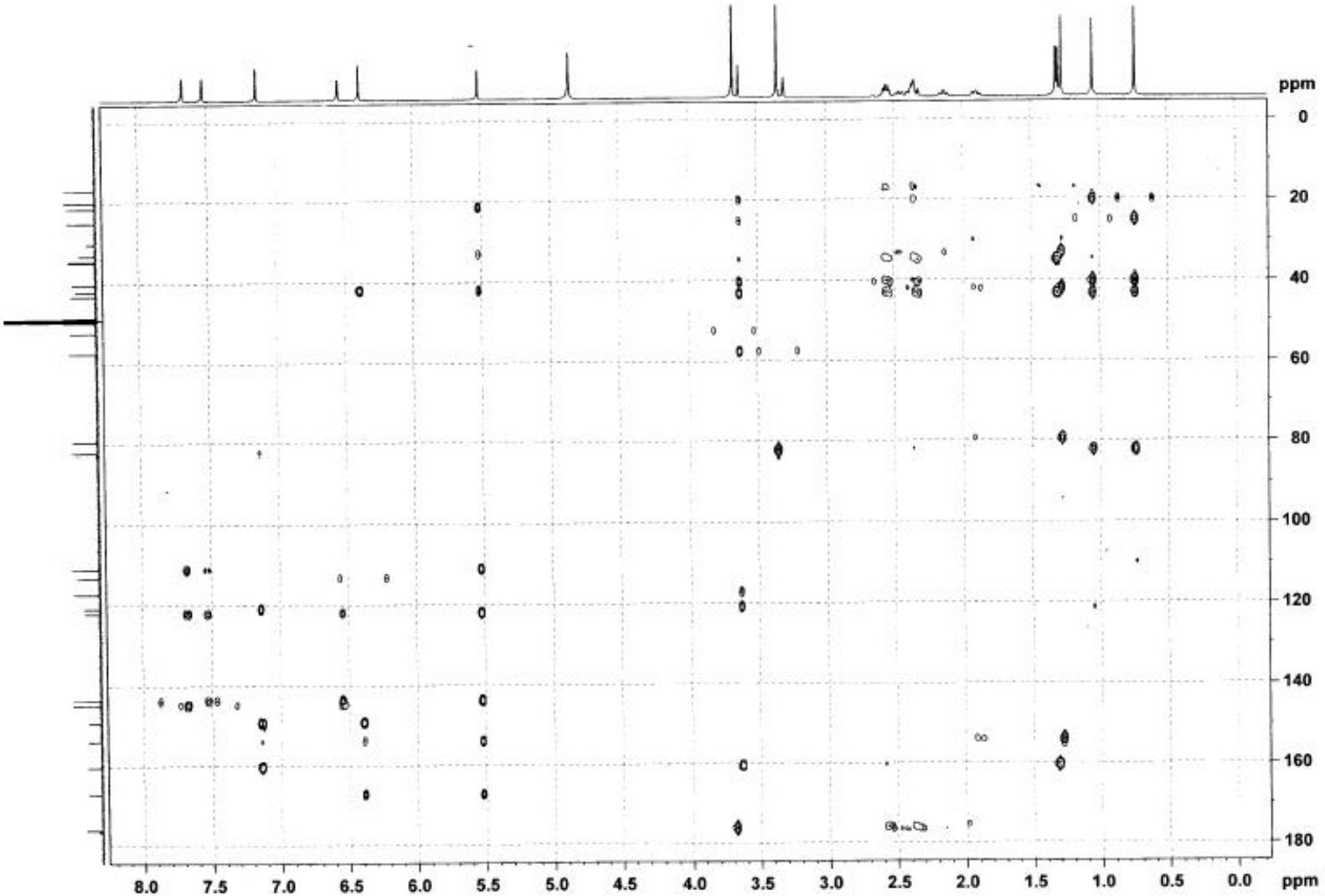
DEPT experiments of xylogranatin K (**6**) in methanol-d_4



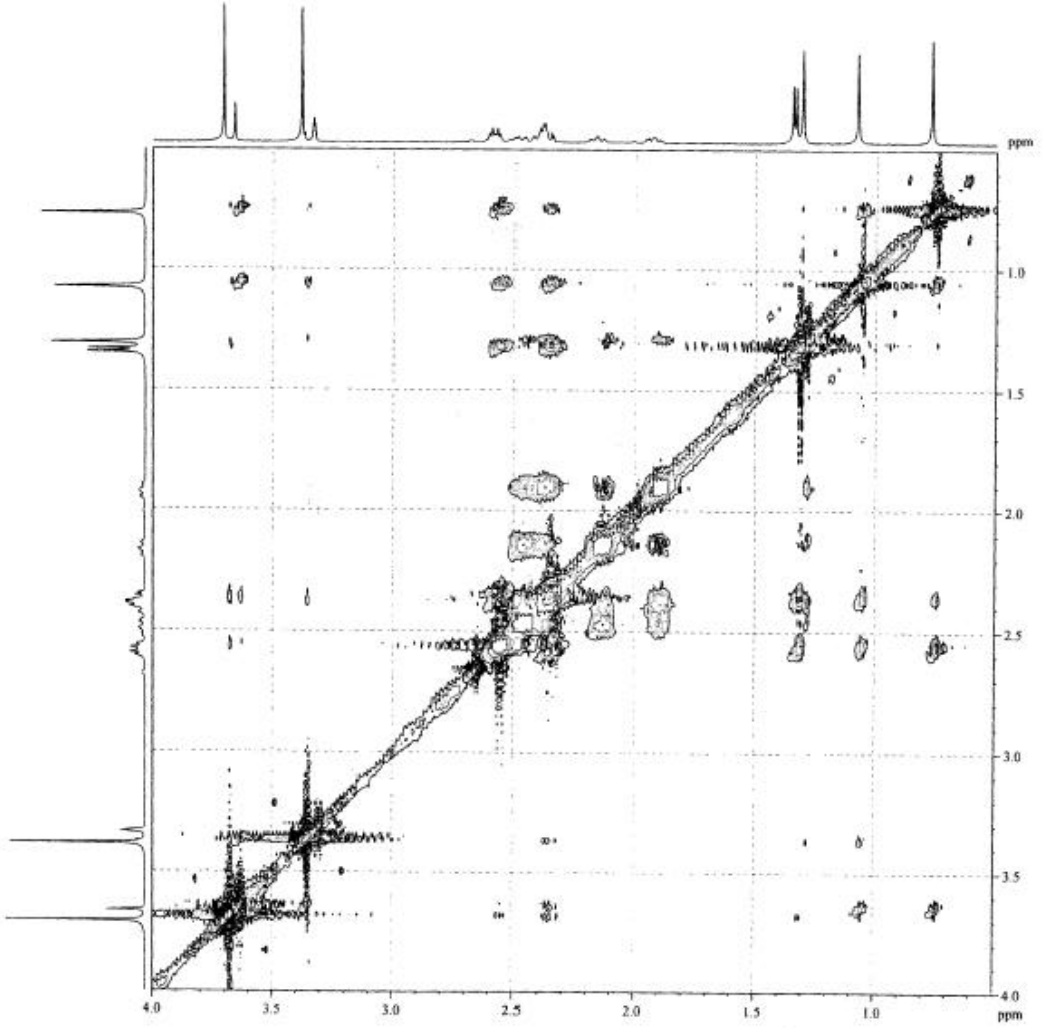
HSQC Spectrum of xylogranatin K (**6**) in methanol-d_4



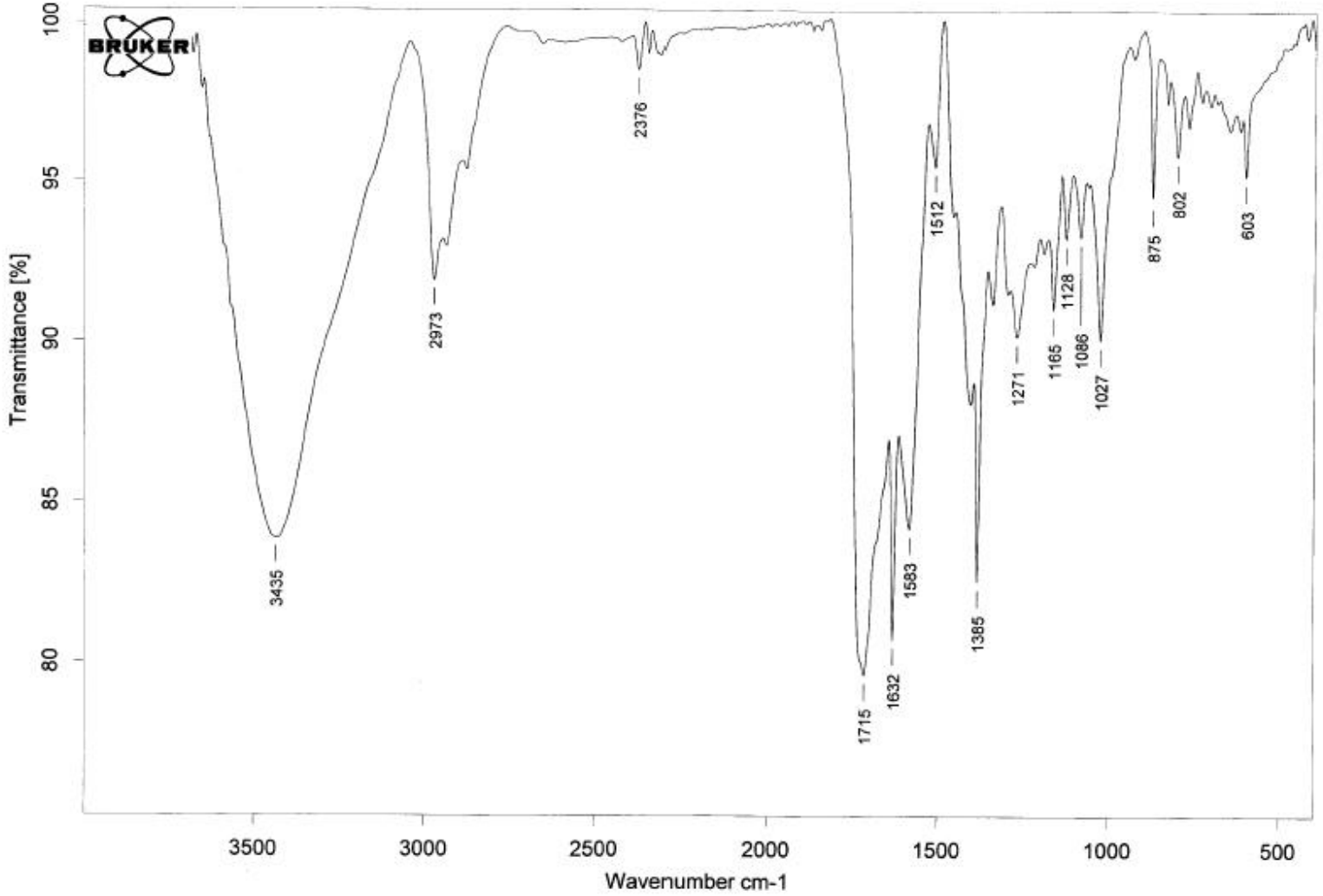
HMBC Spectrum of xylogranatin K (**6**) in methanol-d_4



A Segment of NOESY Spectrum of xylogranatin K (**6**) in methanol-d_4



IR spectrum of xylogranatin L (**7**)



HR-TOFMS of xylogranatin L (**7**)

Elemental Composition Report

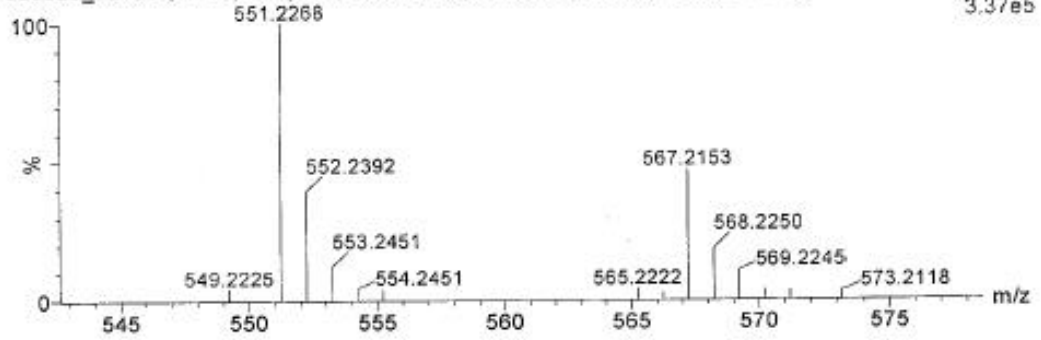
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
55 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

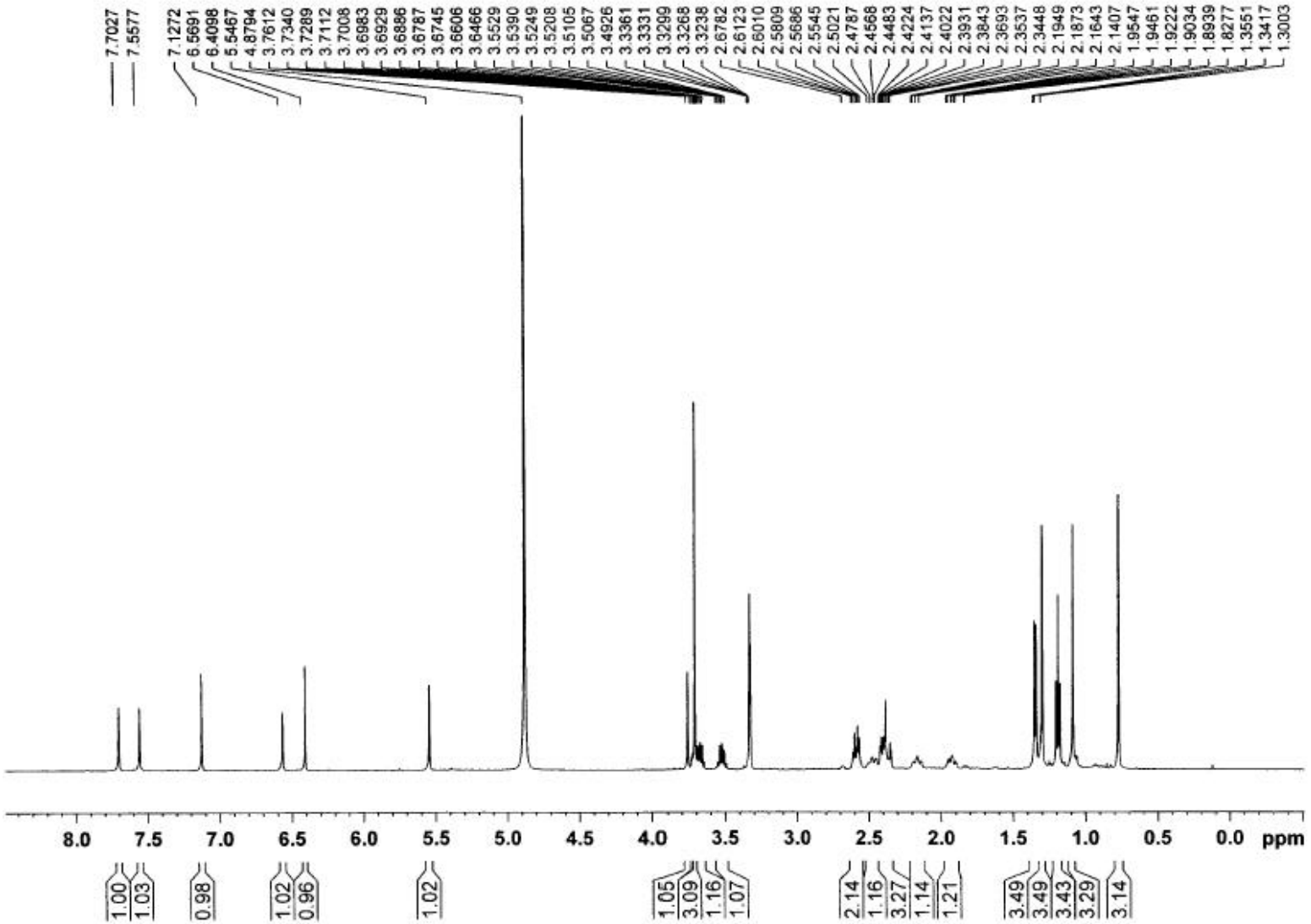
Minimum:				-1.5		
Maximum:		200.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
551.2268	551.2257	1.1	2.0	11.5	2	C29 H36 O9 23Na
	551.2281	-1.3	-2.4	14.5	1	C31 H35 O9

Wu04

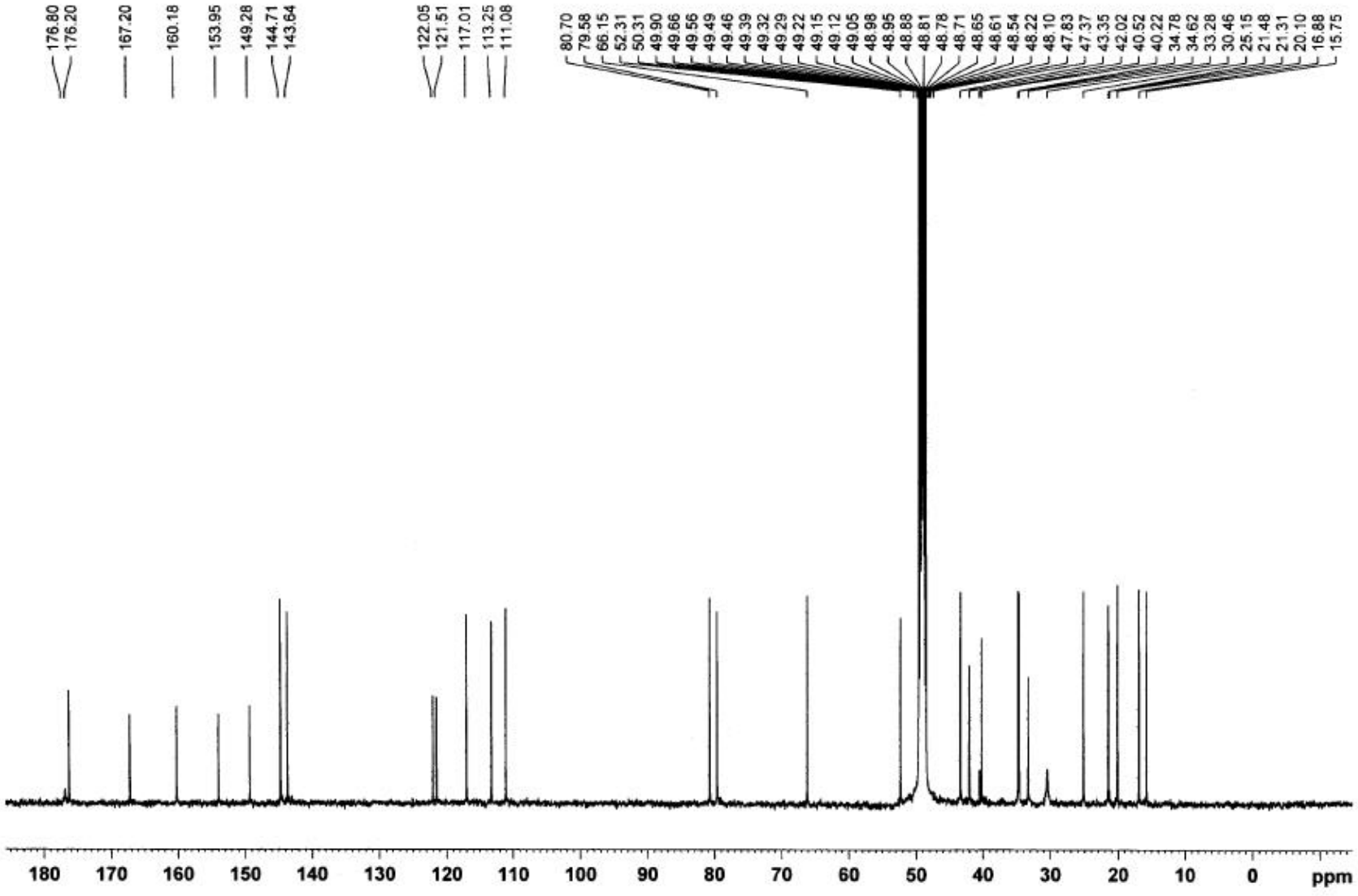
060929_12 90 (1.718) Cn (Cen,4, 80.00, Ar); Sm (SG, 2x3.00); Cm (77:114) TOF MS ES+ 3.37e5



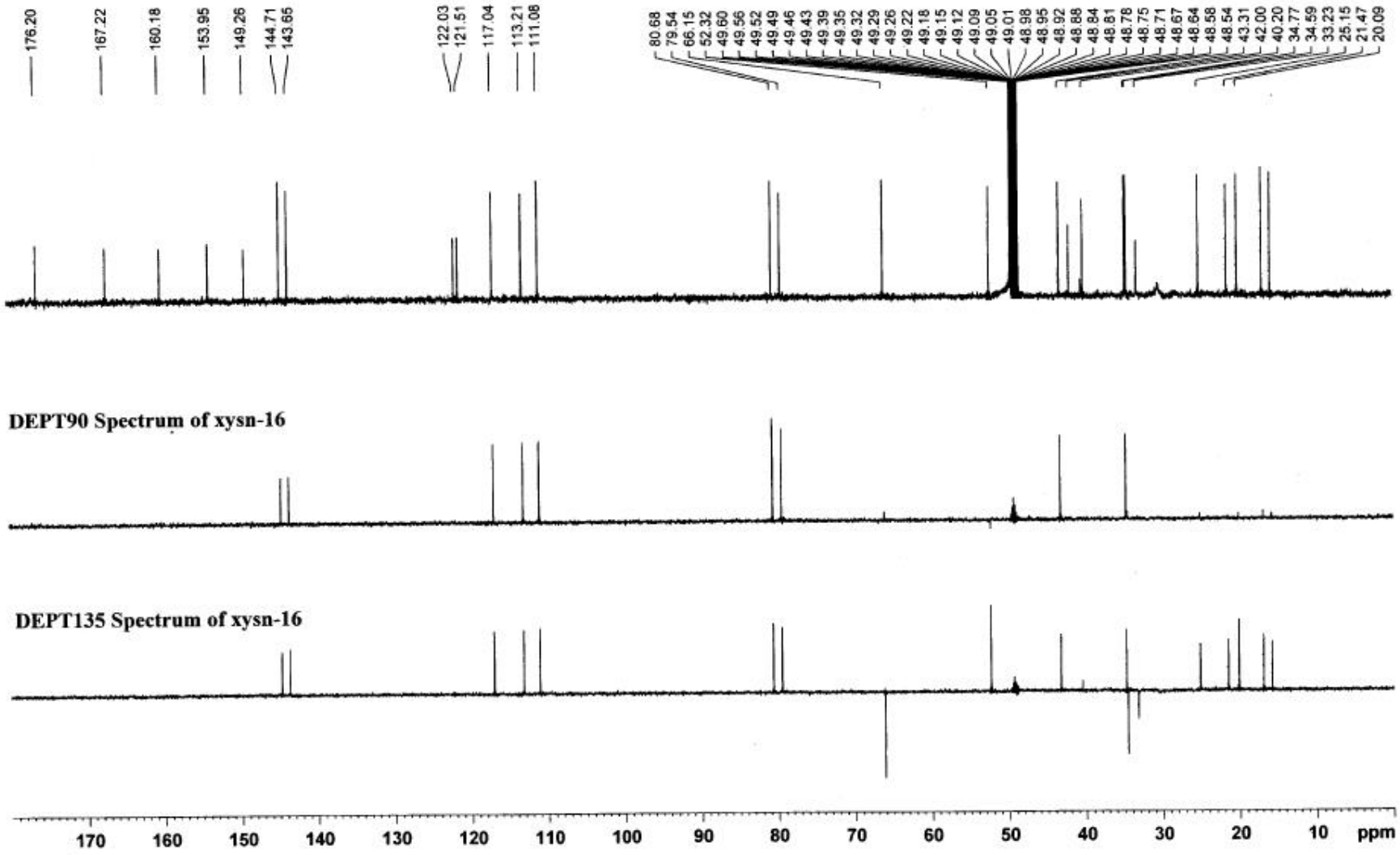
^{1}H NMR (500 MHz) Spectrum of xylogranatin L (**7**) in methanol-d_4



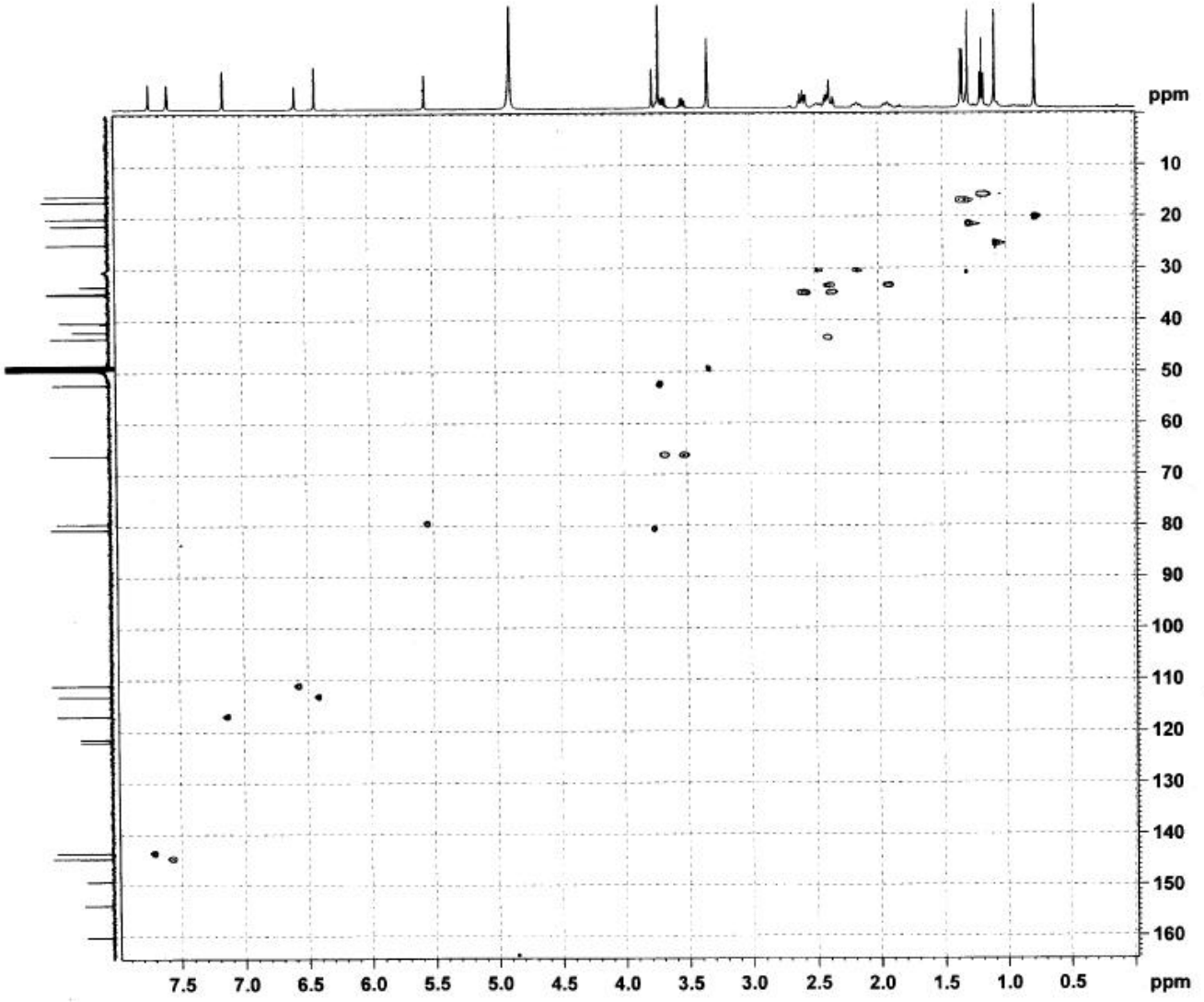
^{13}C NMR (125 MHz) Spectrum of xylogranatin L (**7**) in methanol-d_4



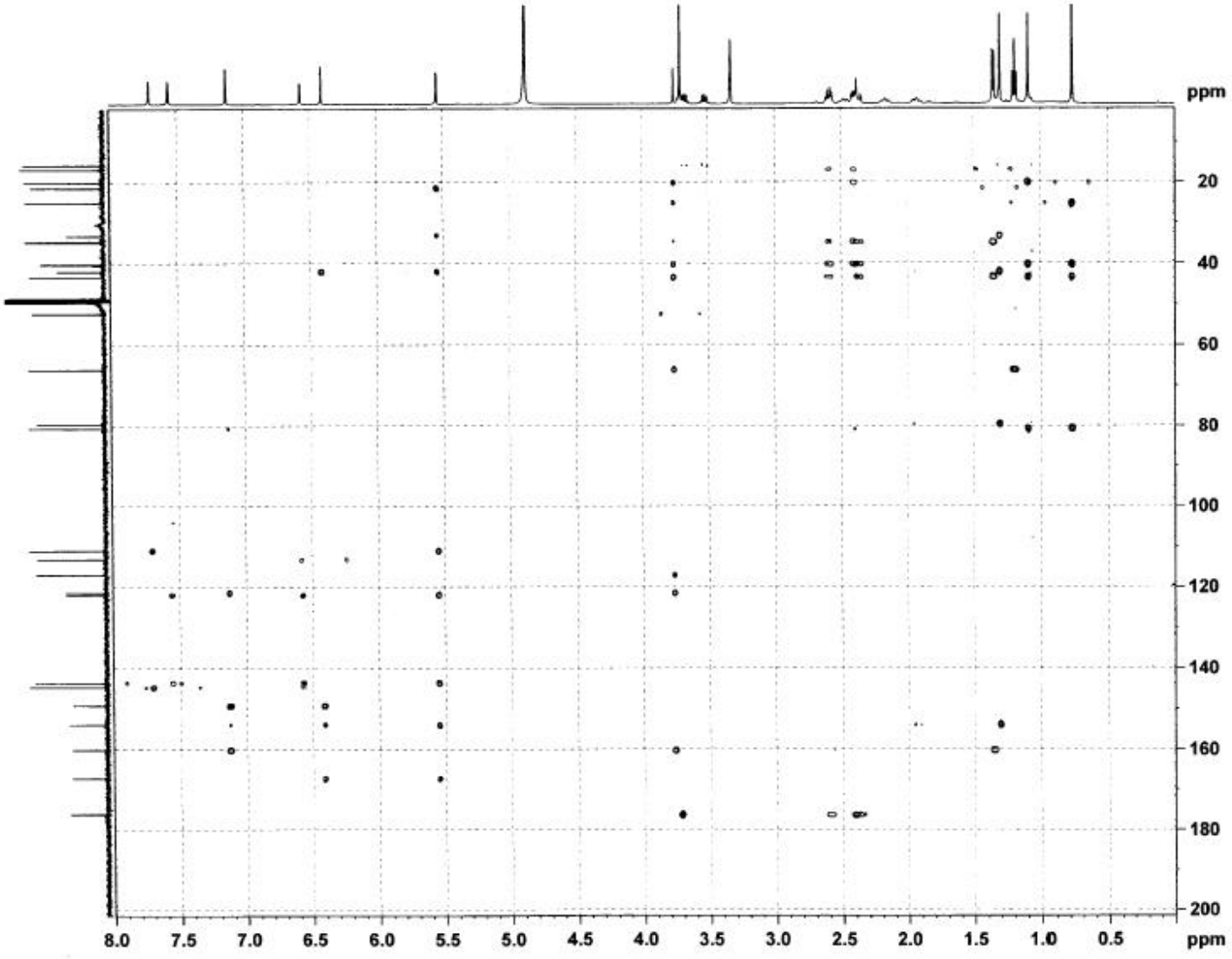
DEPT experiments of xylogranatin L (**7**) in methanol-d_4



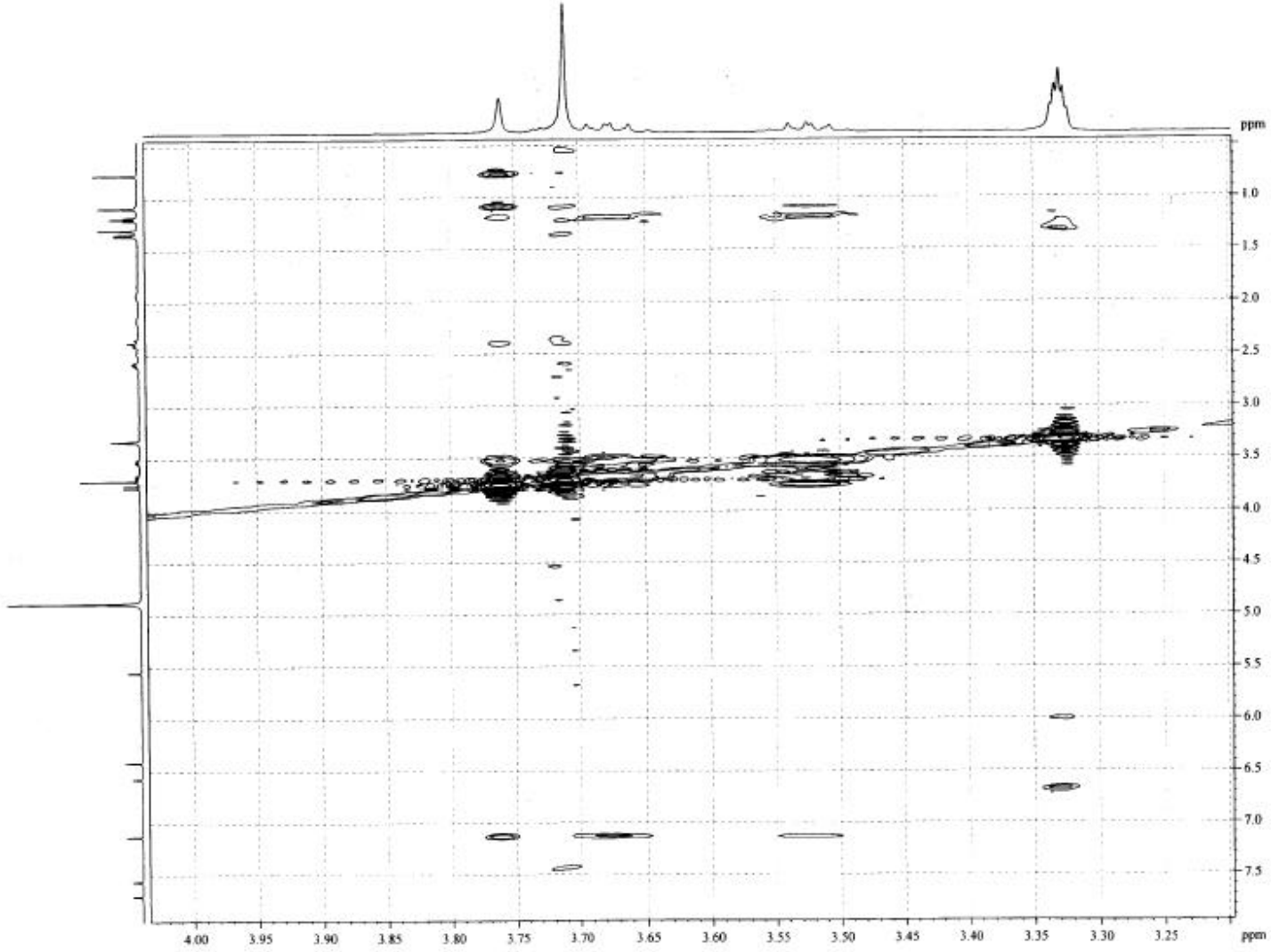
HSQC Spectrum of xylogranatin L (**7**) in methanol-d_4



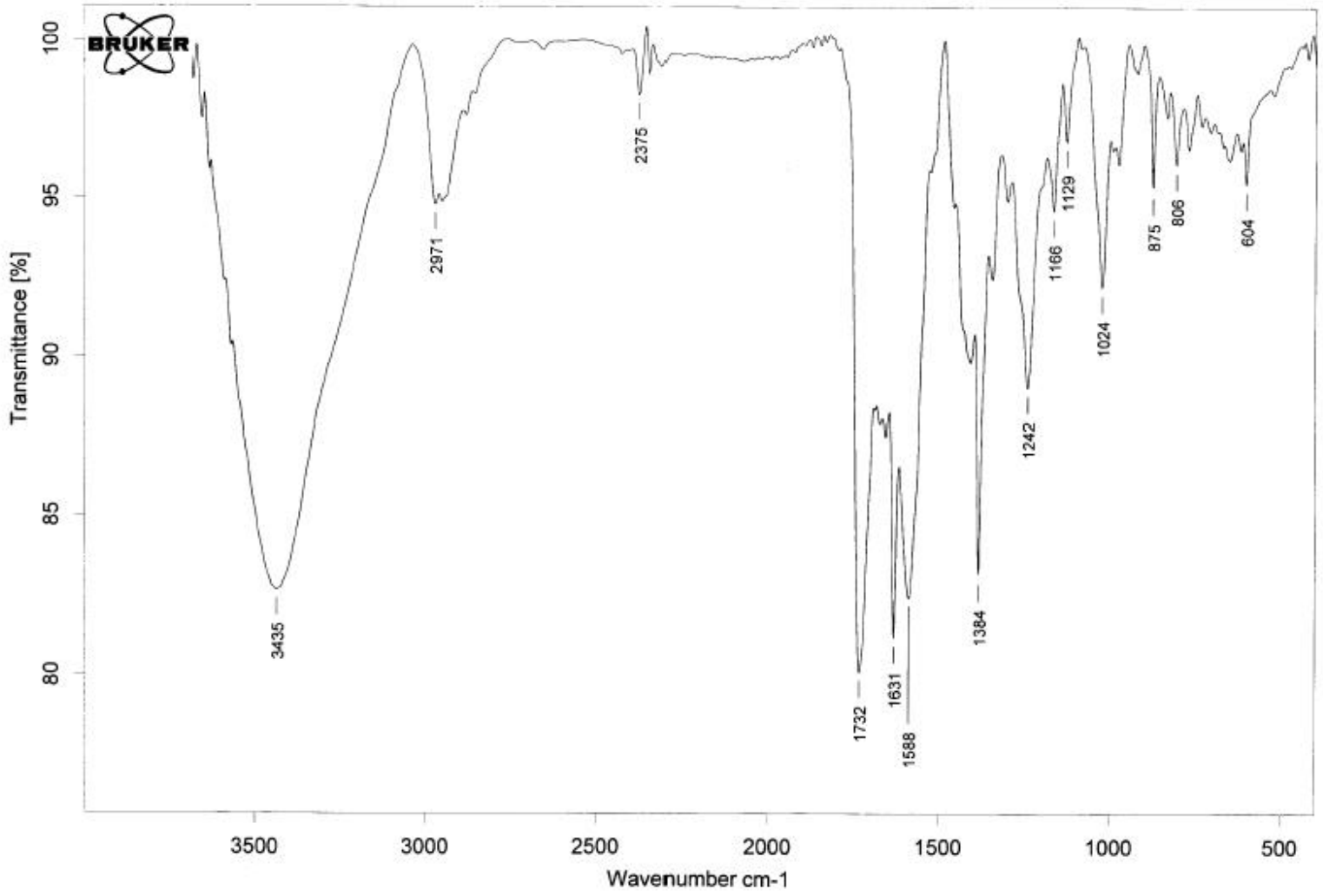
HMBC Spectrum of xylogranatin L (**7**) in methanol-d_4



A Segment of NOESY Spectrum of xylogranatin L (**7**) in methanol-d_4



IR spectrum of xylogranatin M (**8**)



HR-TOFMS of xylogranatin M (**8**)

Elemental Composition Report

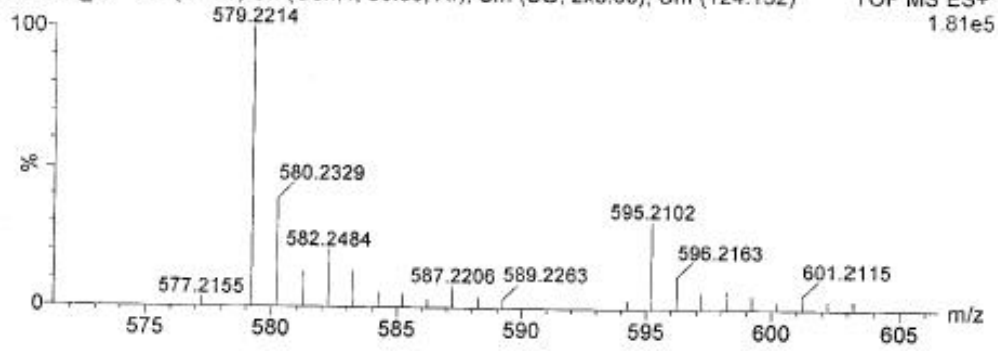
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
45 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

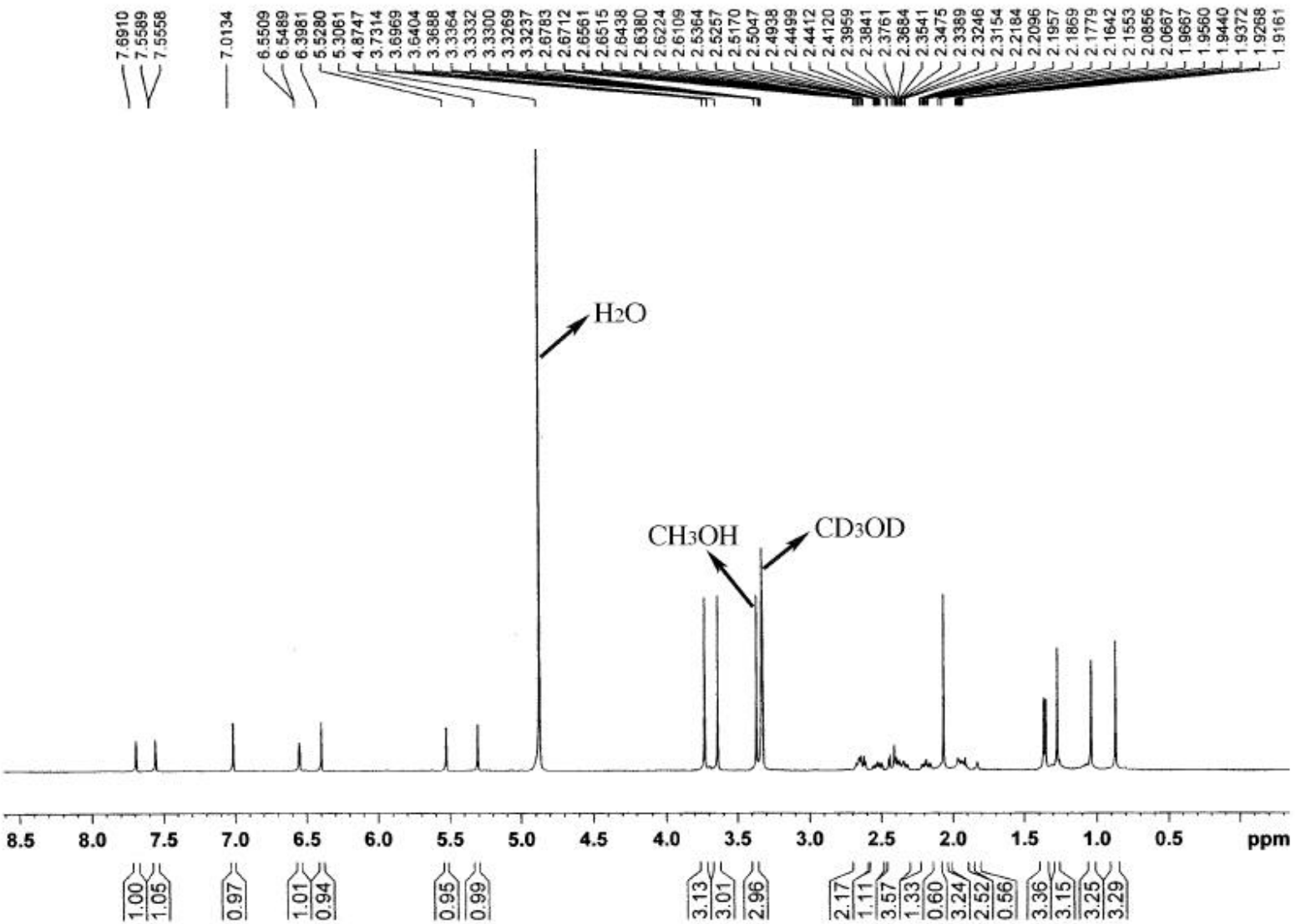
Minimum:				-1.5		
Maximum:		200.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
579.2214	579.2206	0.8	1.4	12.5	2	C30 H36 O10 23Na
	579.2230	-1.6	-2.8	15.5	1	C32 H35 O10

Wu03

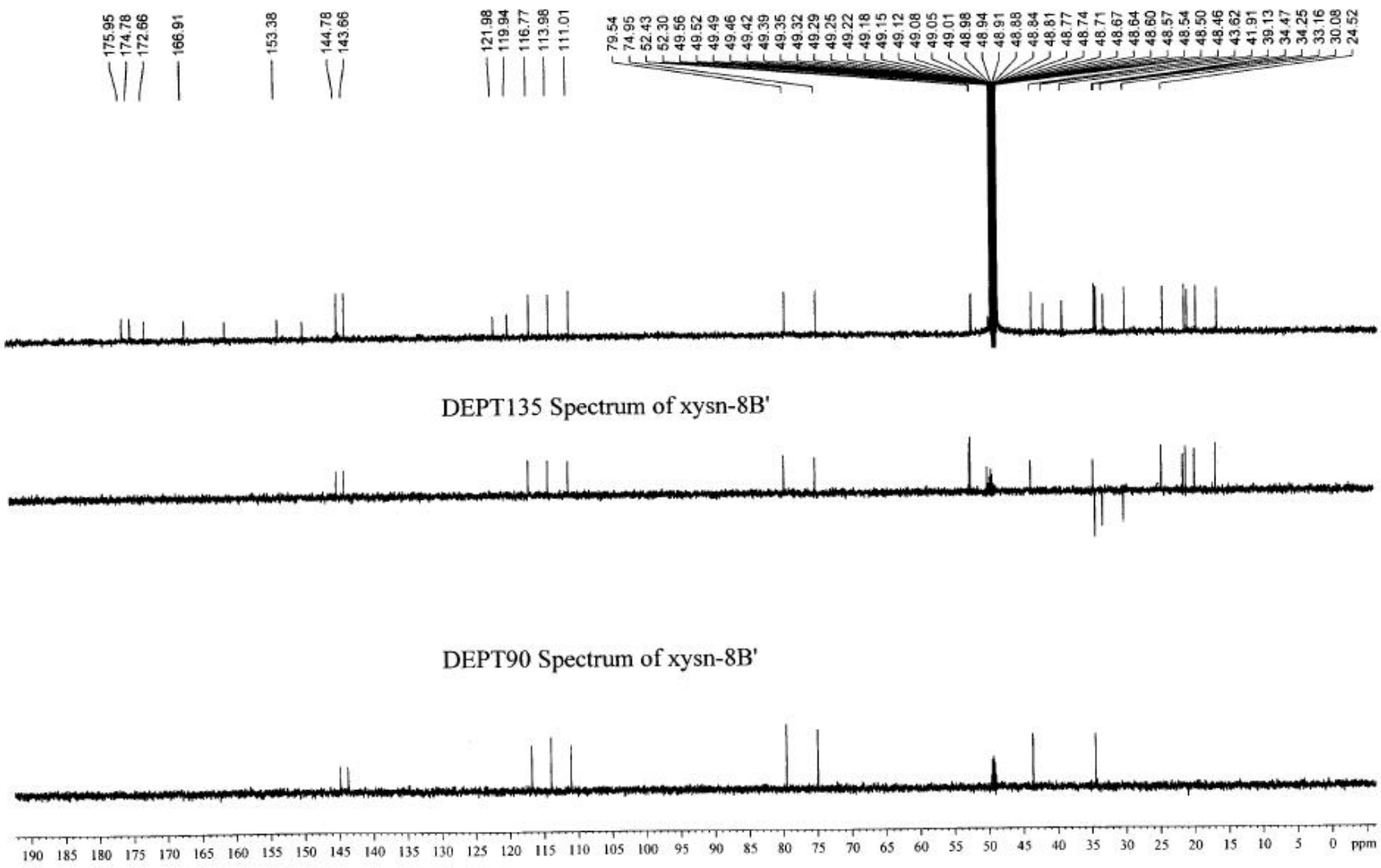
060929_07 125 (2.389) Cn (Cen,4, 80.00, Ar); Sm (SG, 2x3.00); Cm (124:152) TOF MS ES+ 1.81e5



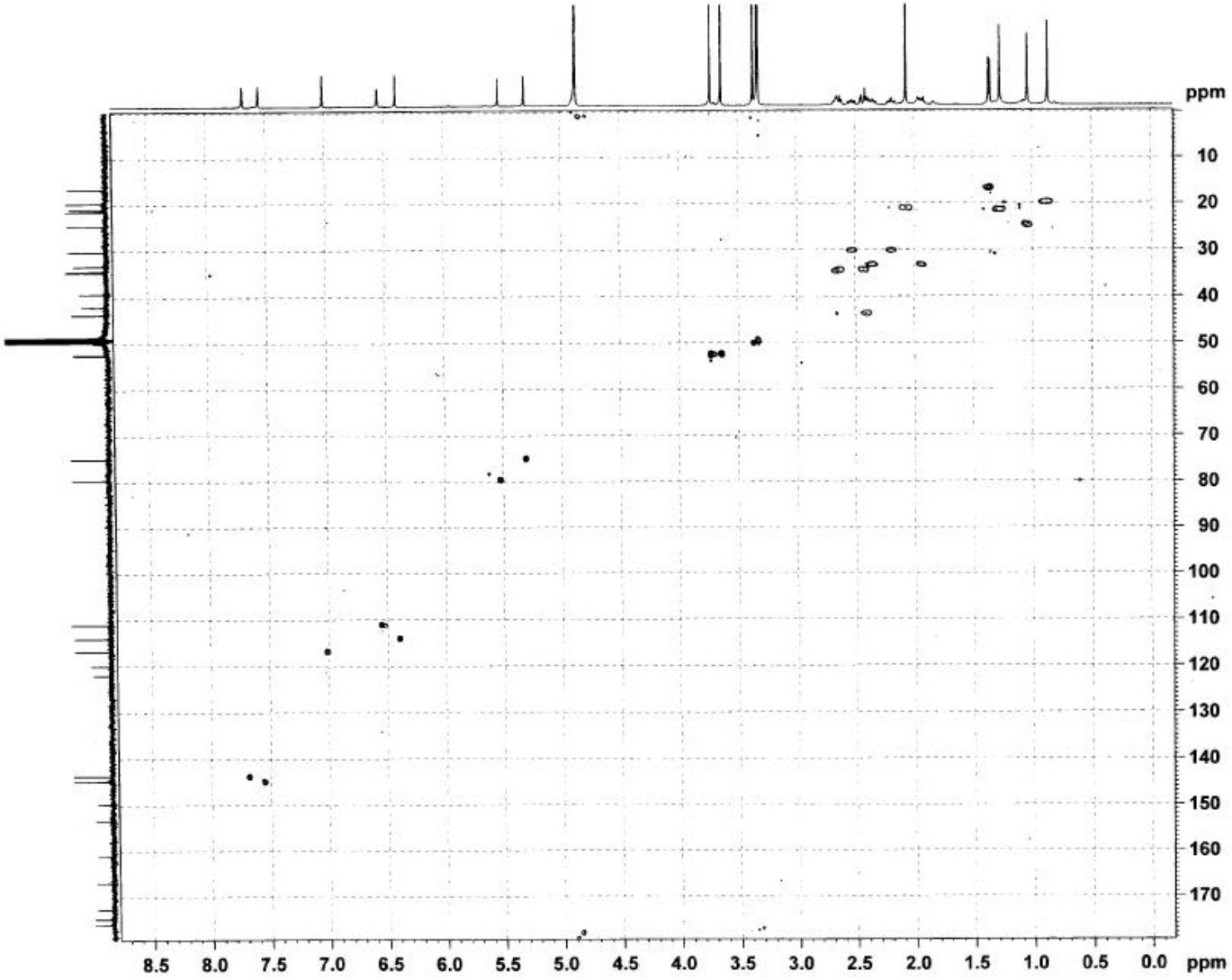
^{1}H NMR (500 MHz) Spectrum of xylogranatin M (**8**) in methanol-d_4



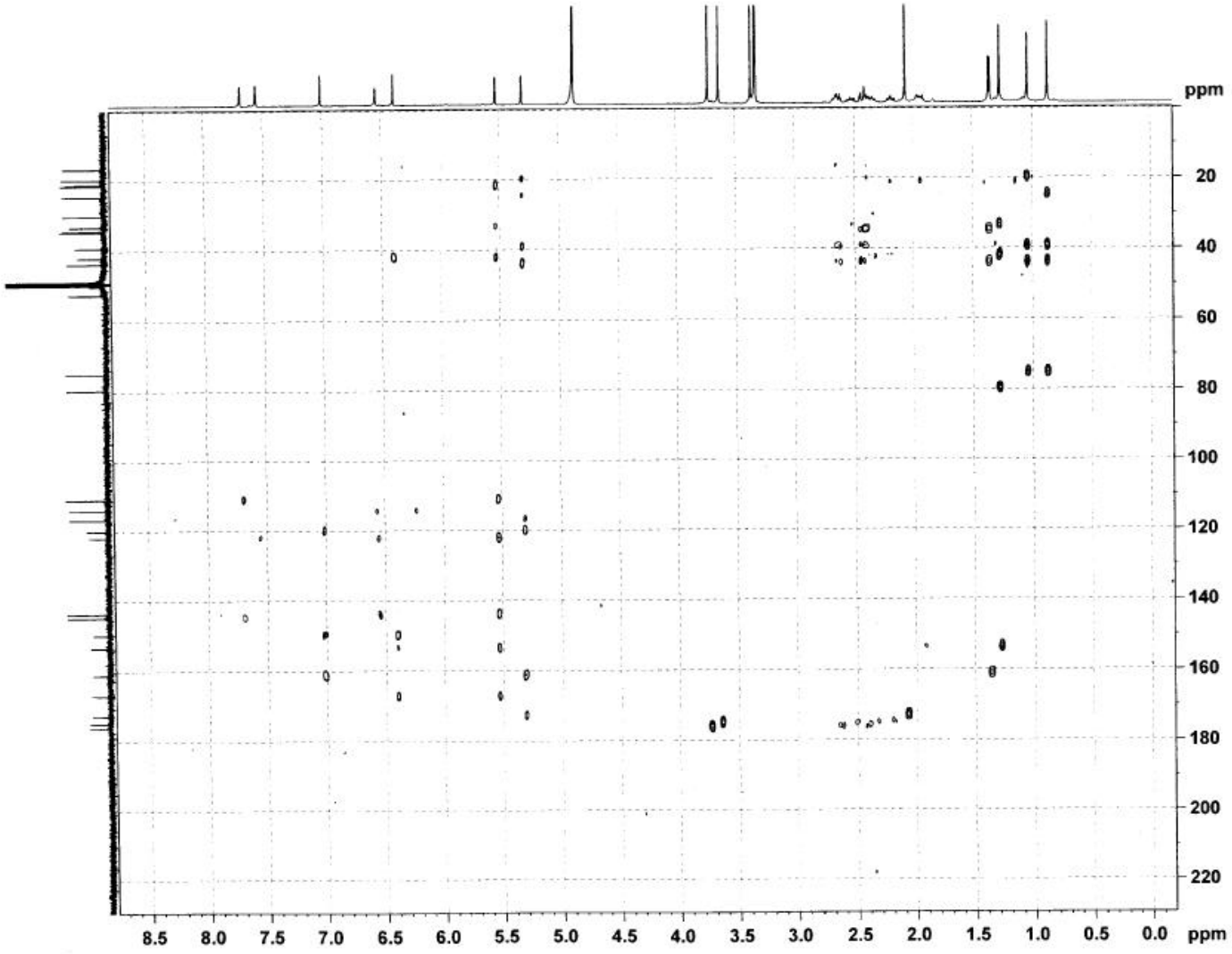
^{13}C NMR (125 MHz) Spectrum and DEPT experiments of xylogranatin M (**8**) in methanol-d_4



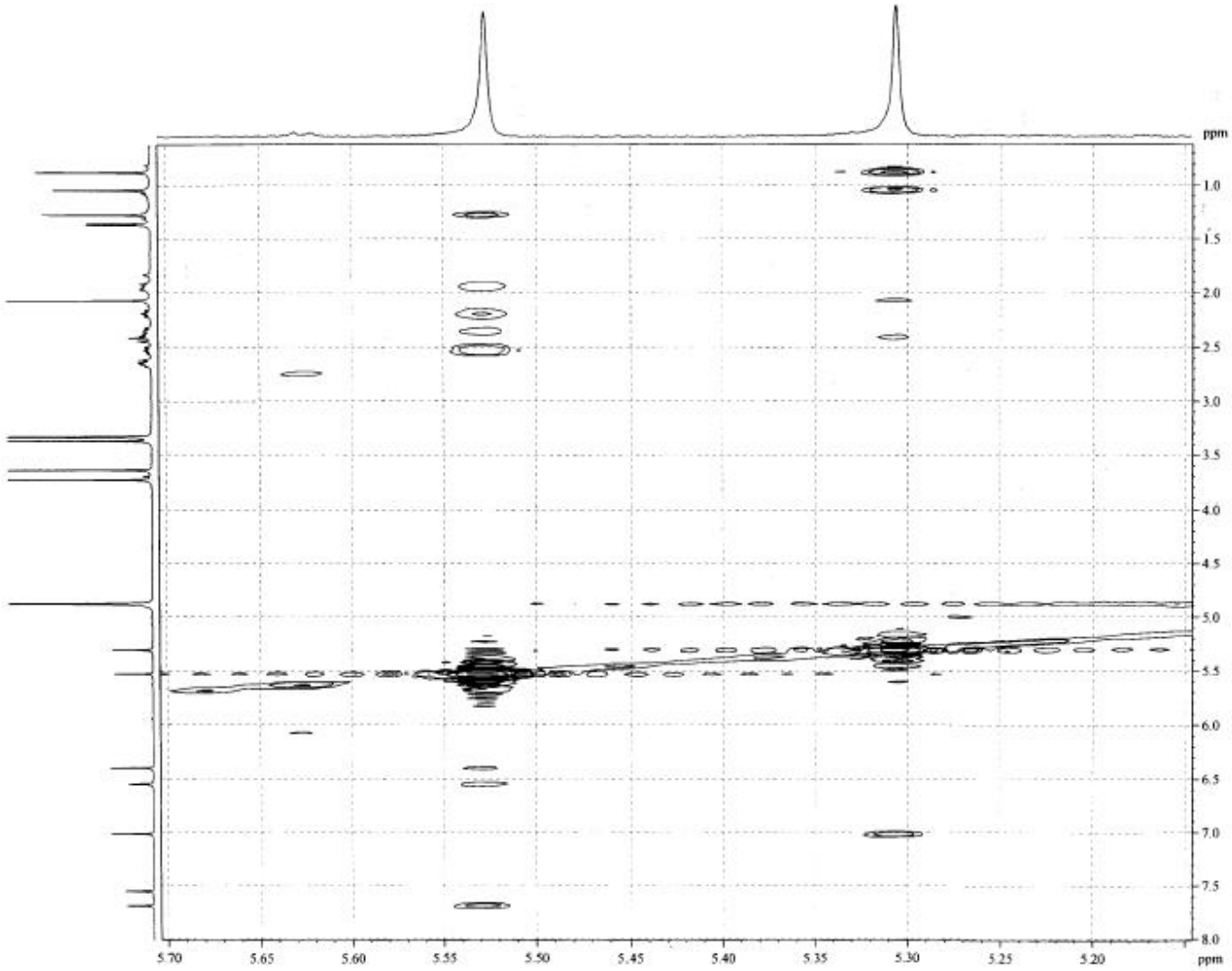
HSQC Spectrum of xylogranatin M (**8**) in methanol-d_4



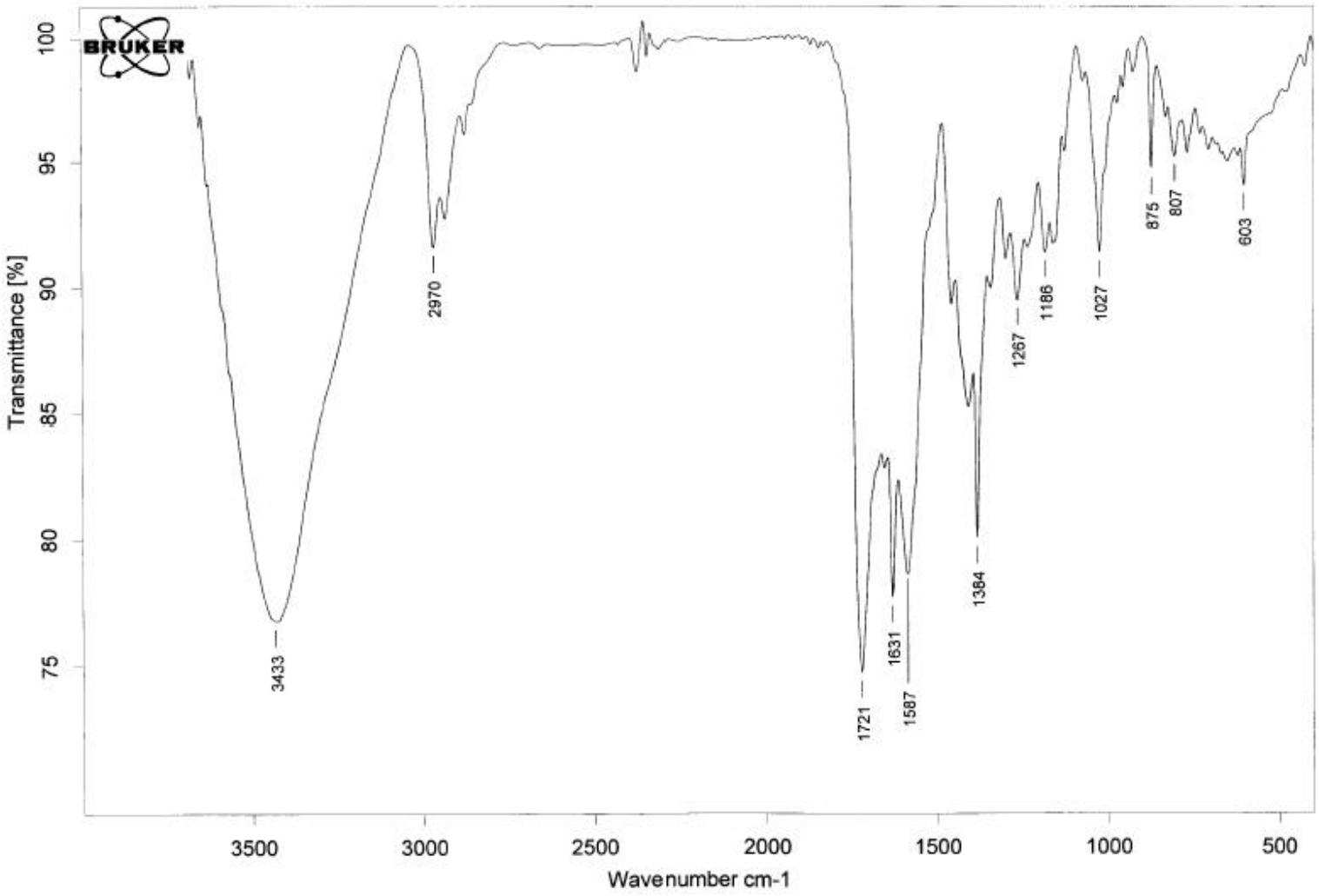
HMBC Spectrum of xylogranatin M (**8**) in methanol-d_4



A Segment of NOESY Spectrum of xylogranatin M (**8**) in methanol-d_4



IR spectrum of xylogranatin N (**9**)



HR-TOFMS of xylogranatin N (**9**)

Elemental Composition Report

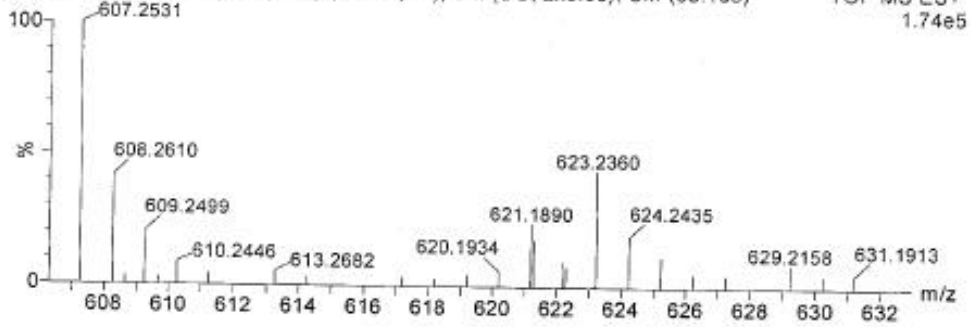
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
35 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

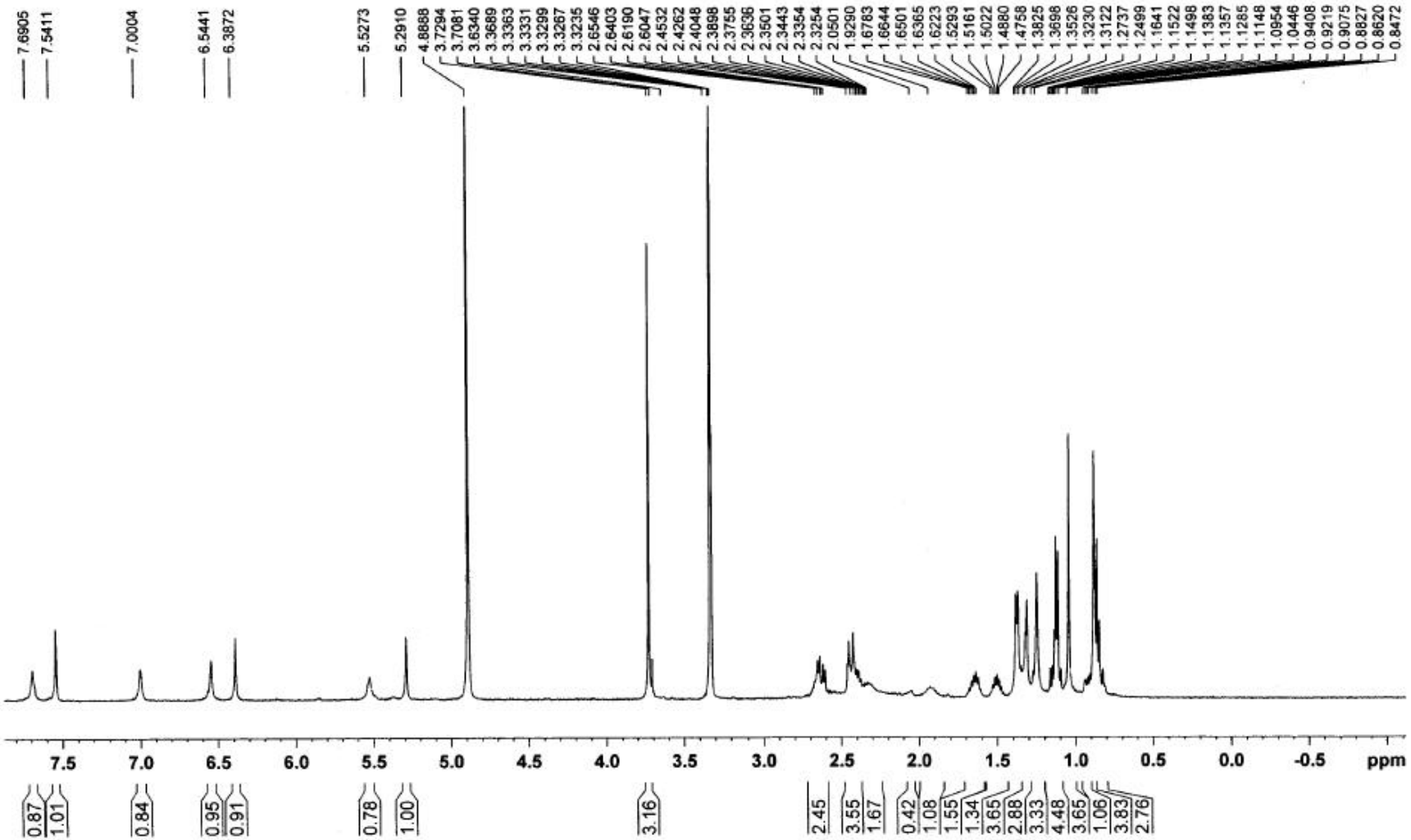
Minimum:				-1.5		
Maximum:		200.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
607.2531	607.2519	1.2	1.9	12.5	2	C32 H40 O10 23Na
	607.2543	-1.2	-2.0	15.5	1	C34 H39 O10

Wu12

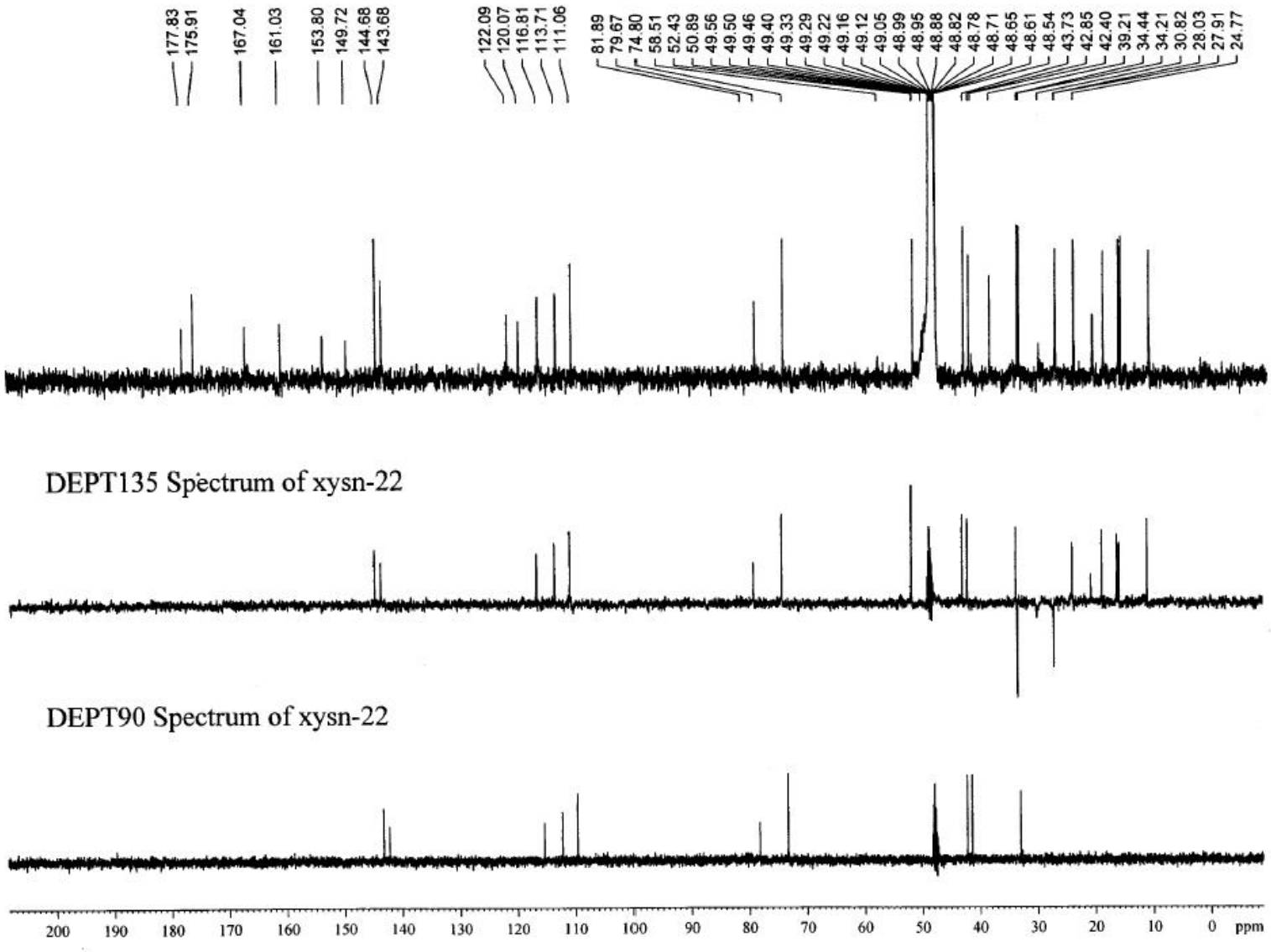
060929_14 96 (1.847) Cn (Cen,4, 80.00, Ar); Sm (SG, 2x3.00); Cm (58:105) TOF MS ES+ 1.74e5



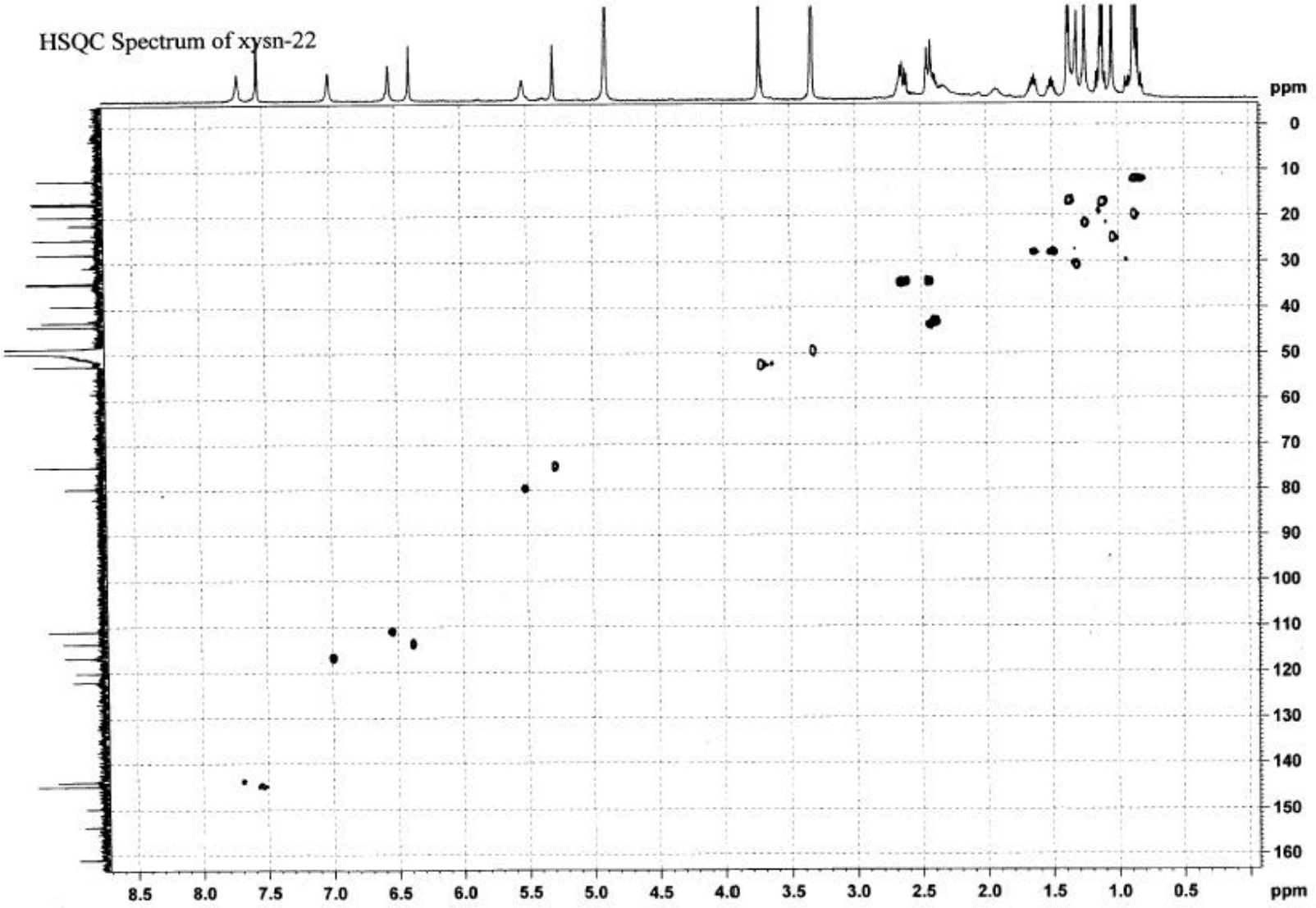
^{1}H NMR (500 MHz) Spectrum of xylogranatin N (**9**) in methanol-d_4



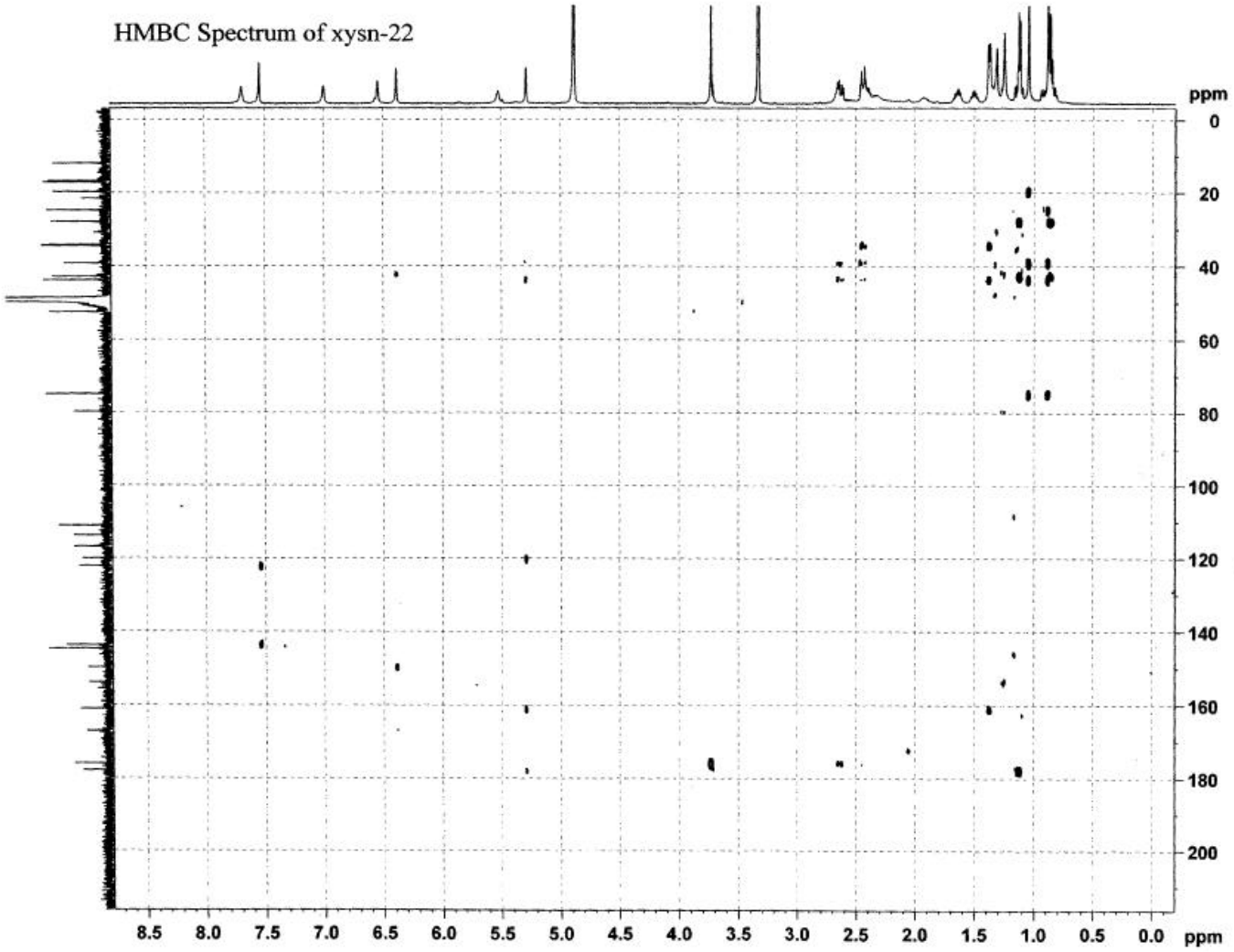
^{13}C NMR (125 MHz) Spectrum and DEPT experiments of xylogranatin N (**9**) in methanol-d_4



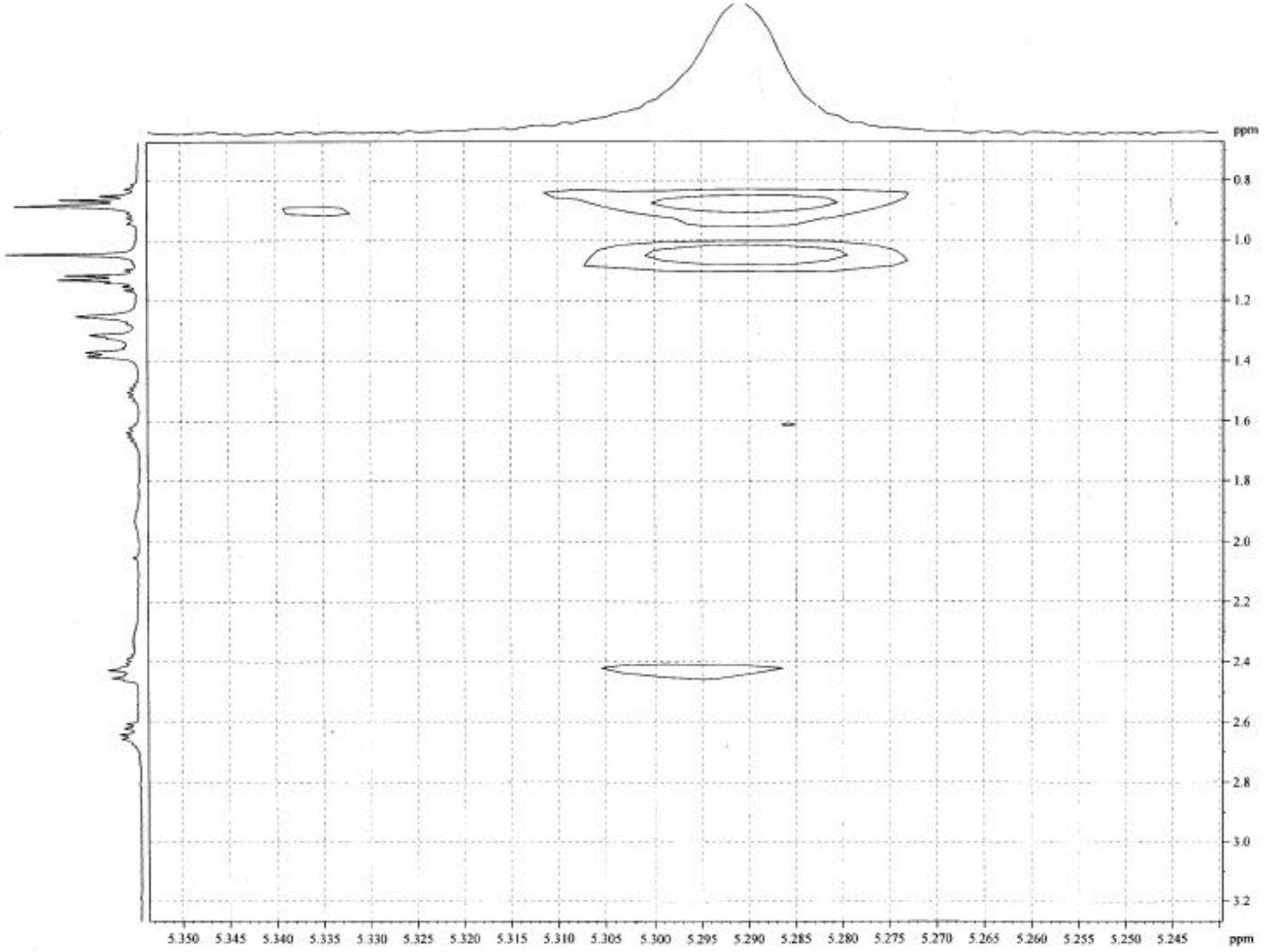
HSQC Spectrum of xylogranatin N (**9**) in methanol-d_4



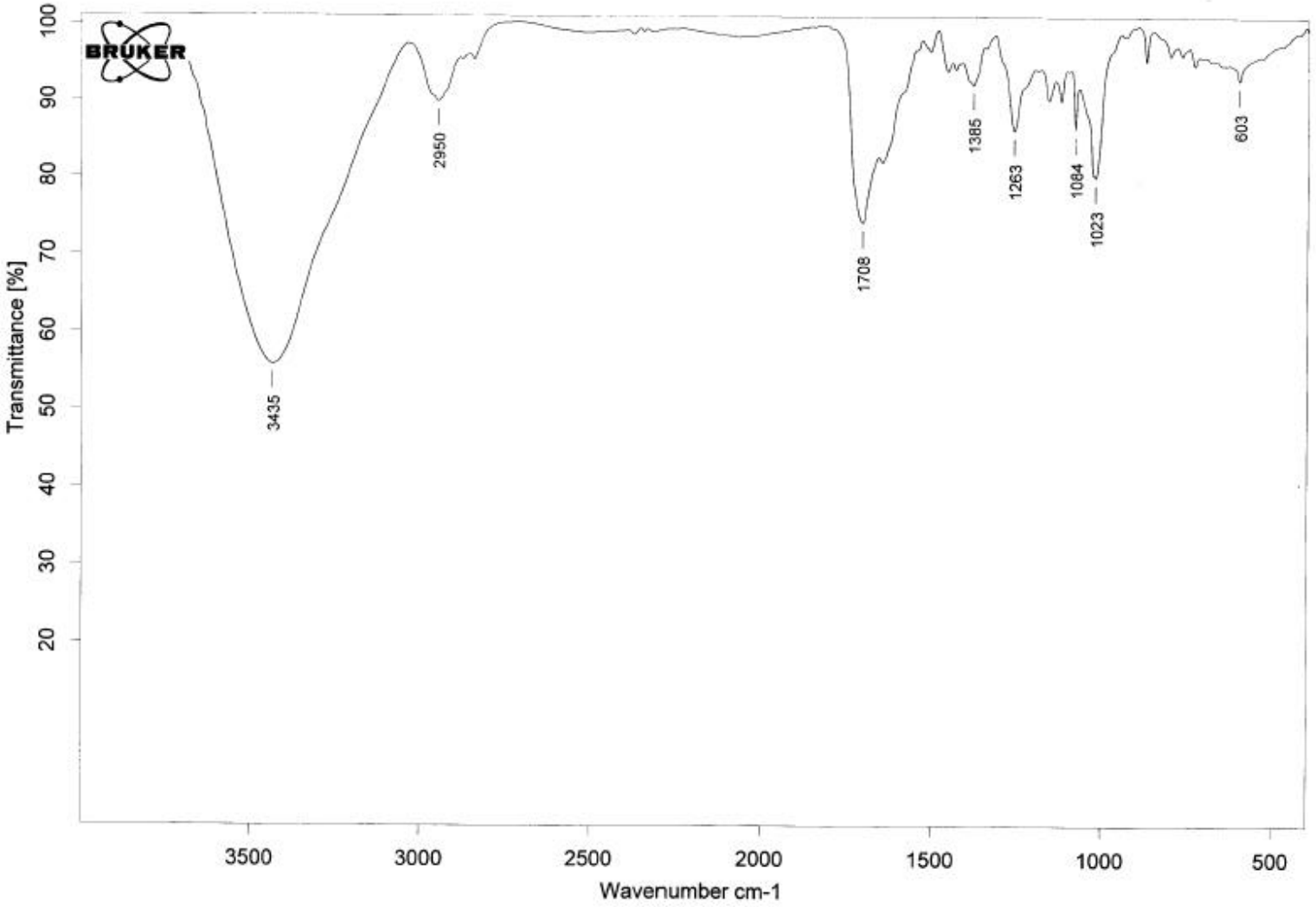
HMBC Spectrum of xylogranatin N (**9**) in methanol-d_4



A Segment of NOESY Spectrum of xylogranatin N (**9**) in methanol-d_4



IR spectrum of xylogranatin O (**10**)



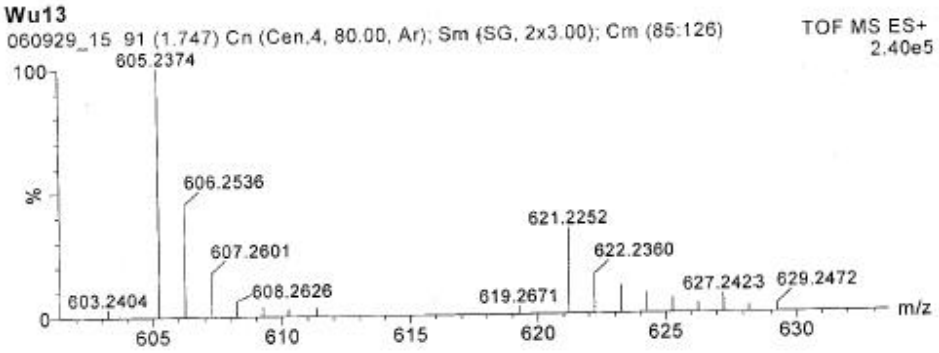
HR-TOFMS of xylogranatin O (**10**)

Elemental Composition Report

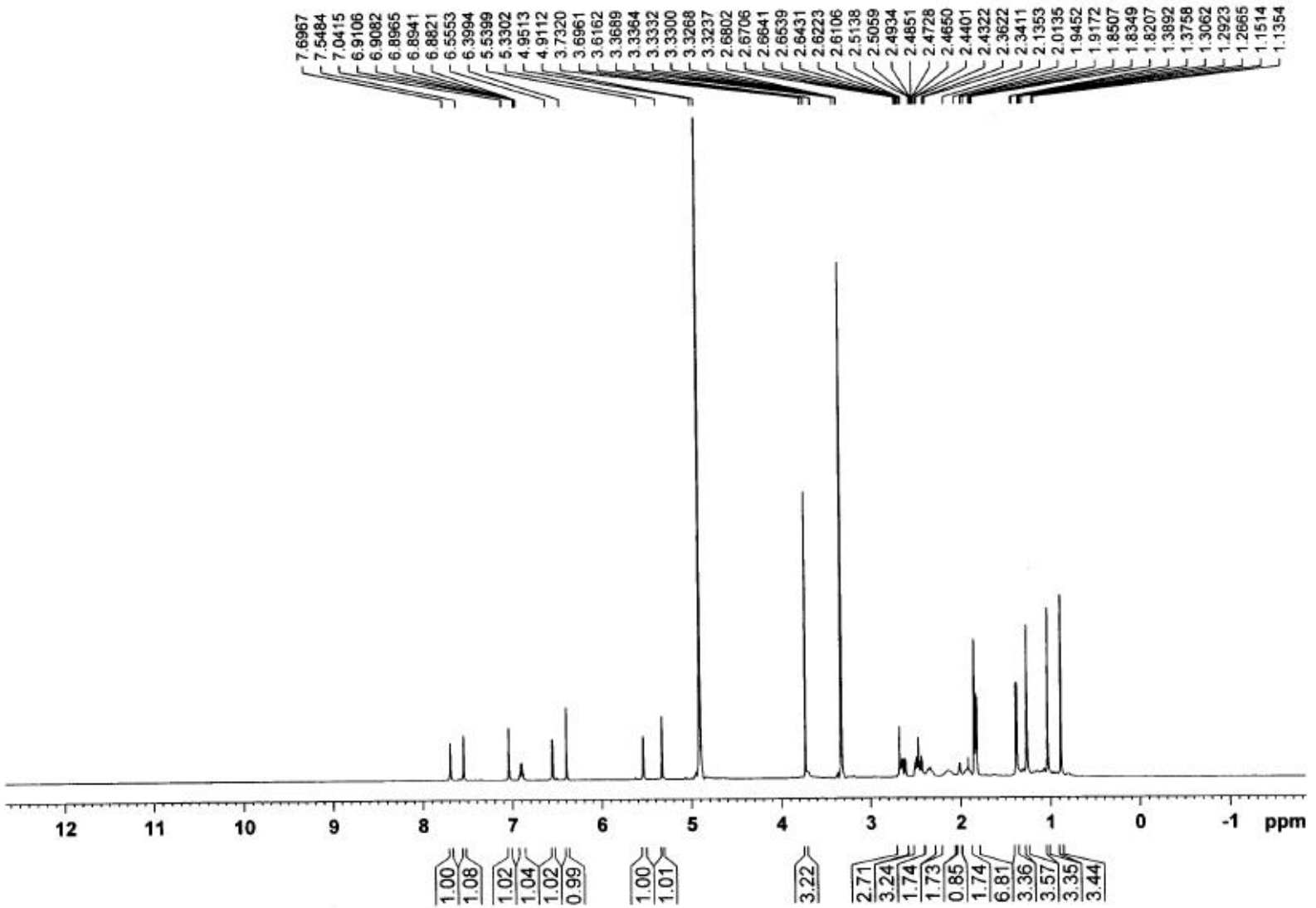
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
34 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

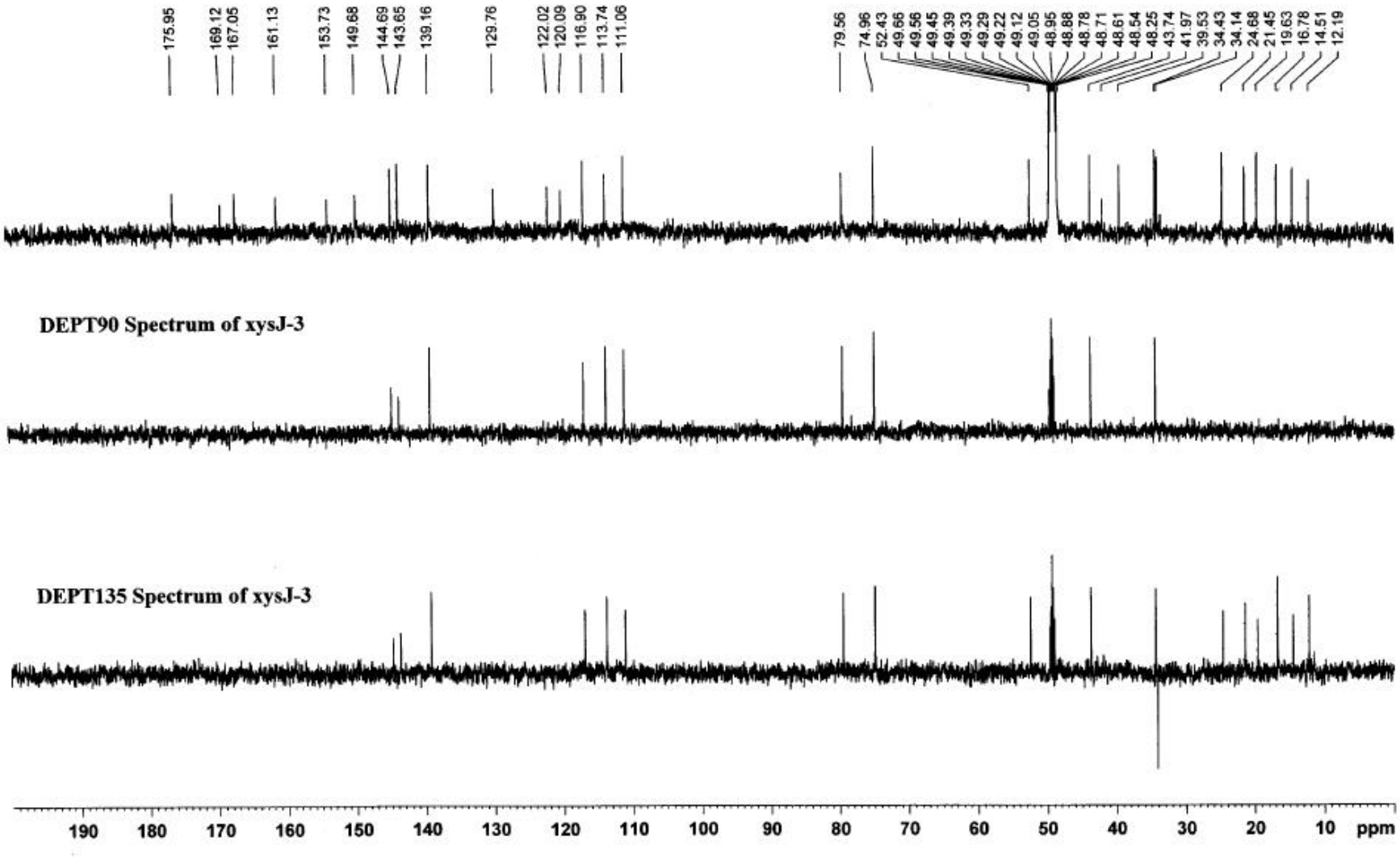
Minimum:				-1.5		
Maximum:		200.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
605.2374	605.2363	1.1	1.9	13.5	2	C32 H38 O10 23Na
	605.2387	-1.3	-2.1	16.5	1	C34 H37 O10



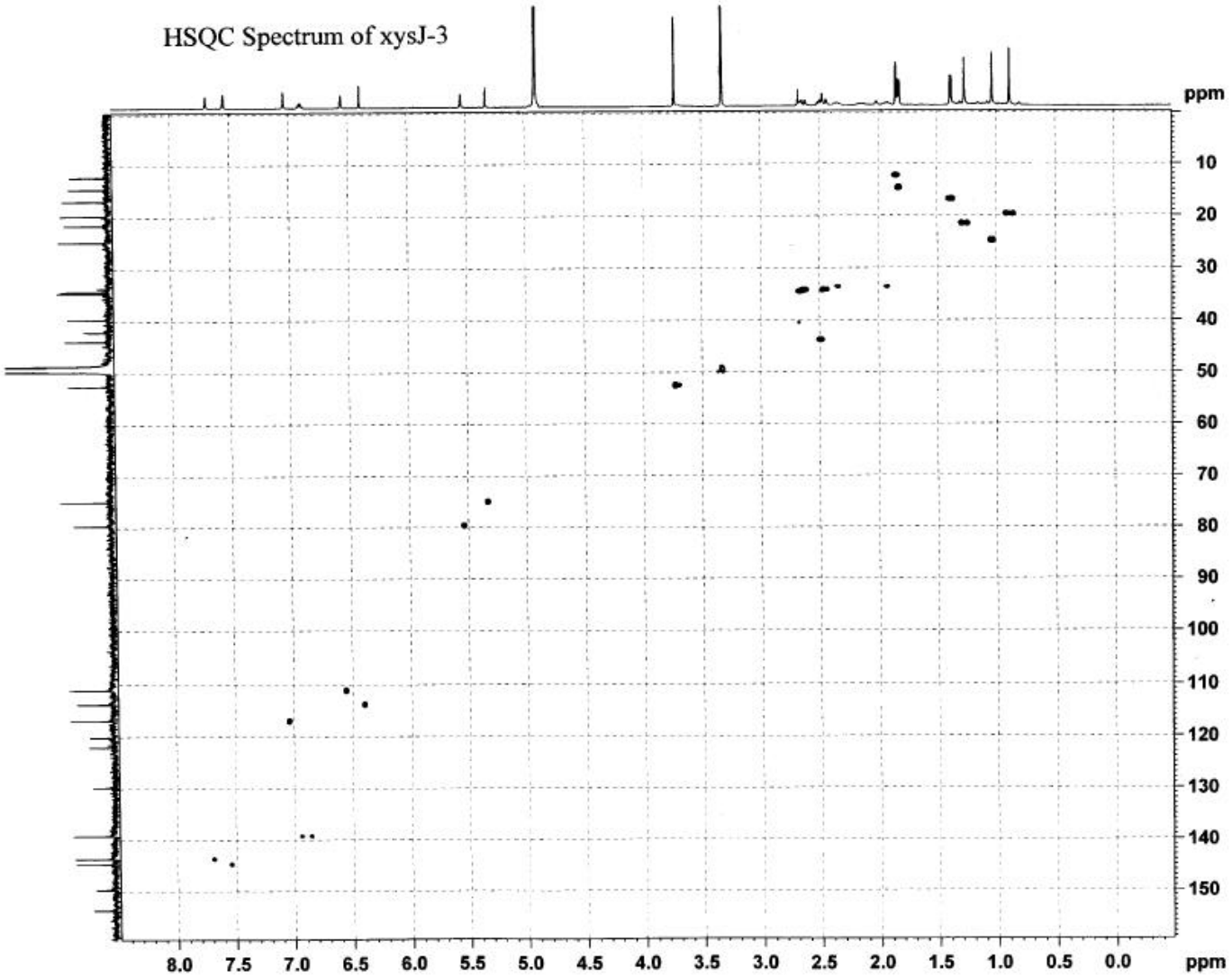
^{1}H NMR (500 MHz) Spectrum of xylogranatin O (**10**) in methanol-d_4



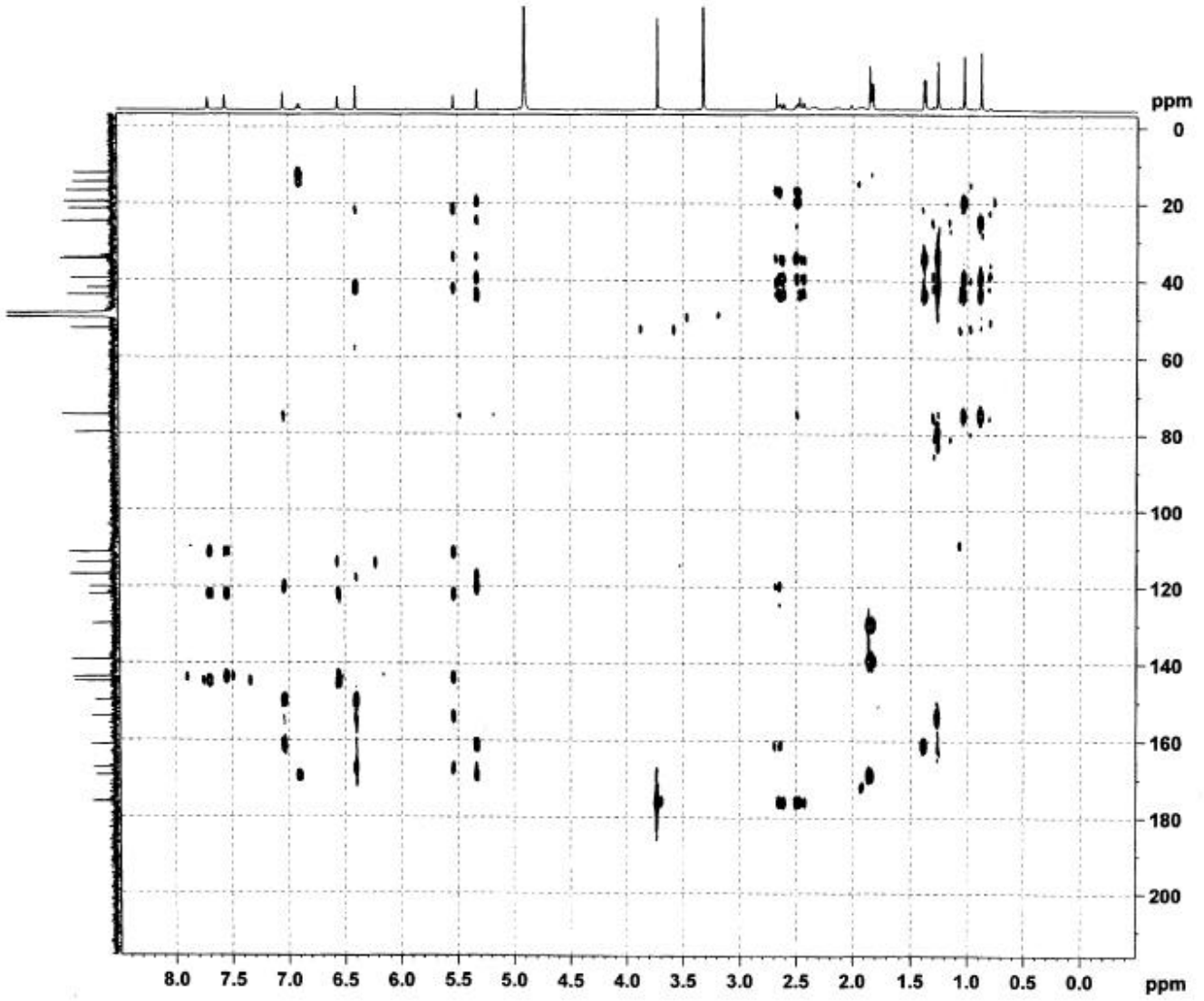
^{13}C NMR (125 MHz) Spectrum and DEPT experiments of xylogranatin O (**10**) in methanol-d_4



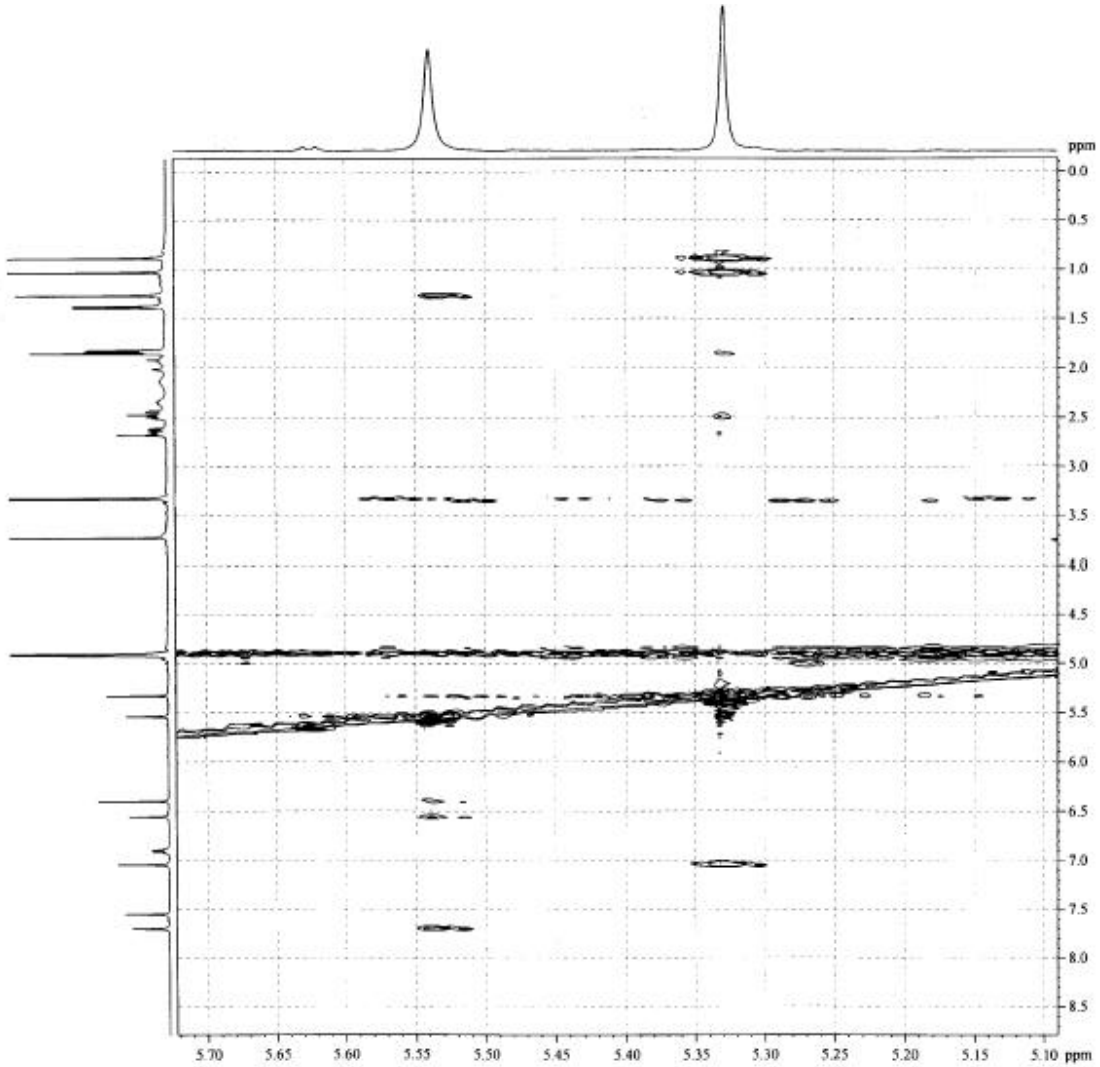
HSQC Spectrum of xylogranatin O (**10**) in methanol-d_4



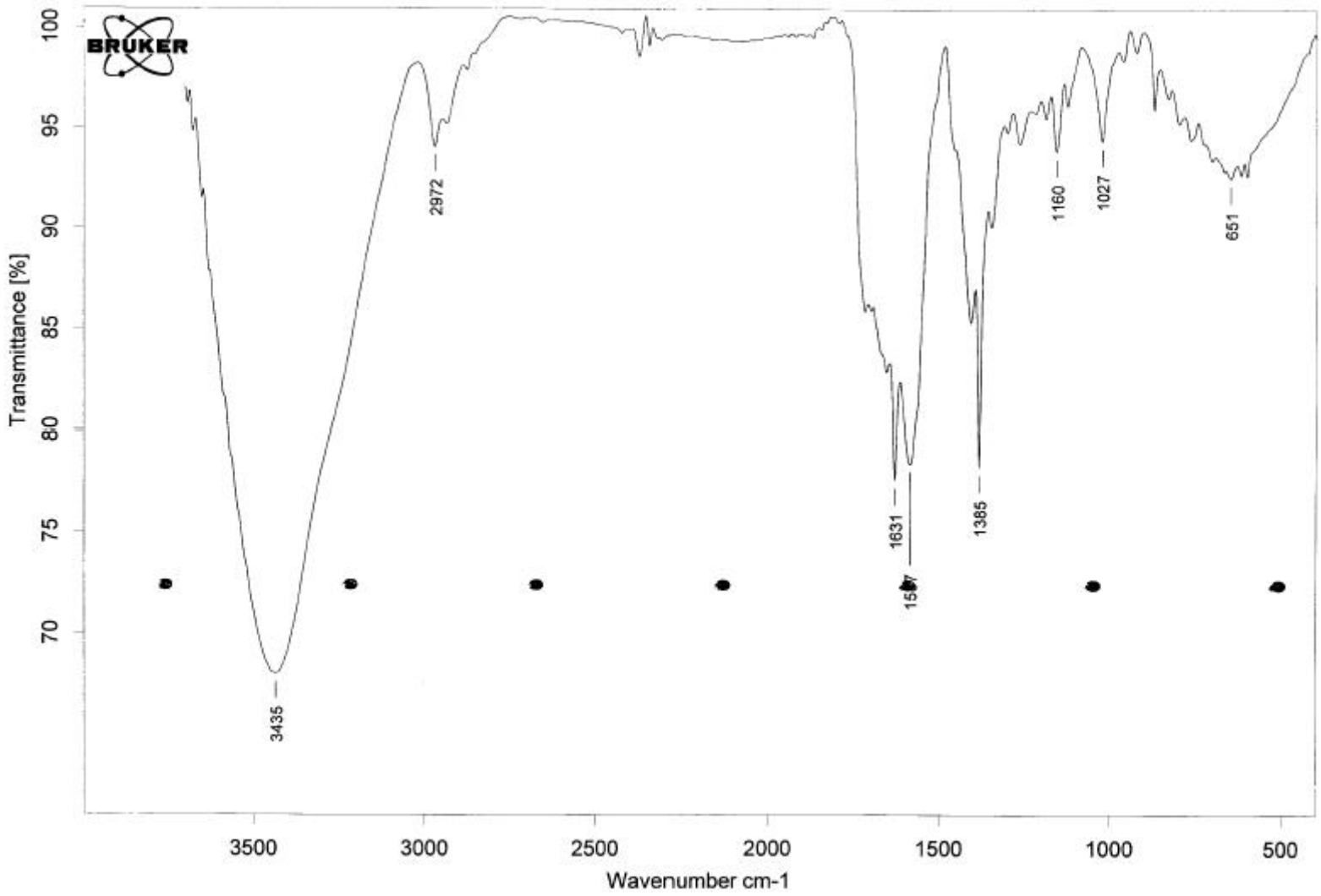
HMBC Spectrum of xylogranatin O (**10**) in methanol-d_4



A Segment of NOESY Spectrum of xylogranatin O (**10**) in methanol-d_4



IR spectrum of xylogranatin P (**11**)



HR-TOFMS of xylogranatin P (**11**)

Elemental Composition Report

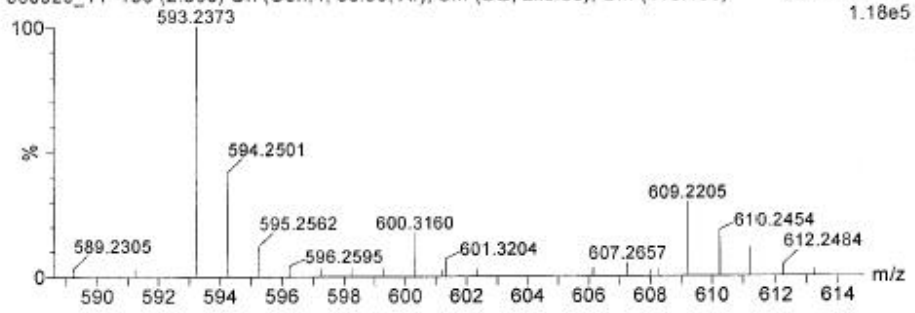
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
37 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

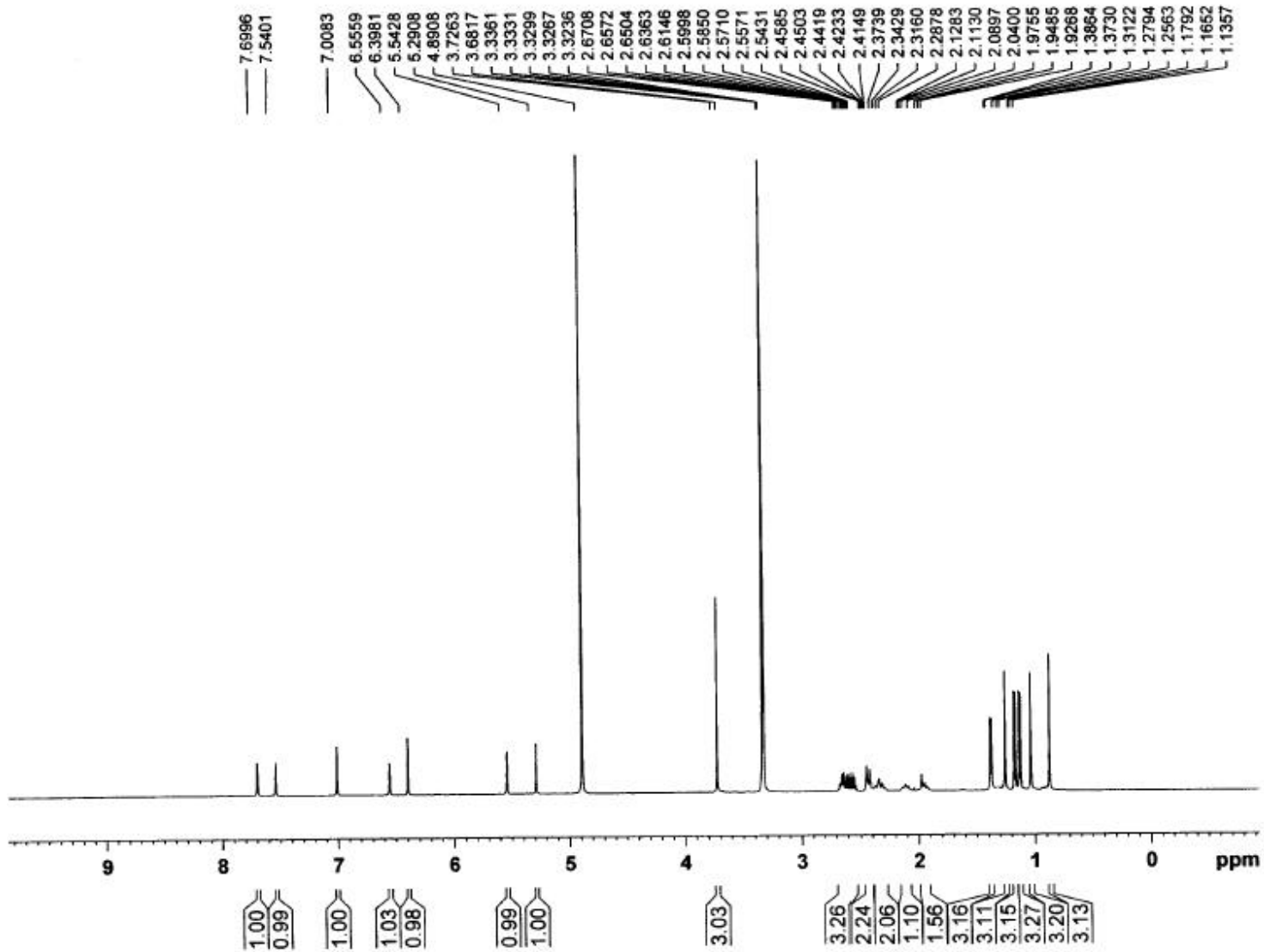
Minimum:				-1.5		
Maximum:		200.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
593.2373	593.2363	1.0	1.7	12.5	2	C31 H38 O10 23Na
	593.2387	-1.4	-2.3	15.5	1	C33 H37 O10

Wu01

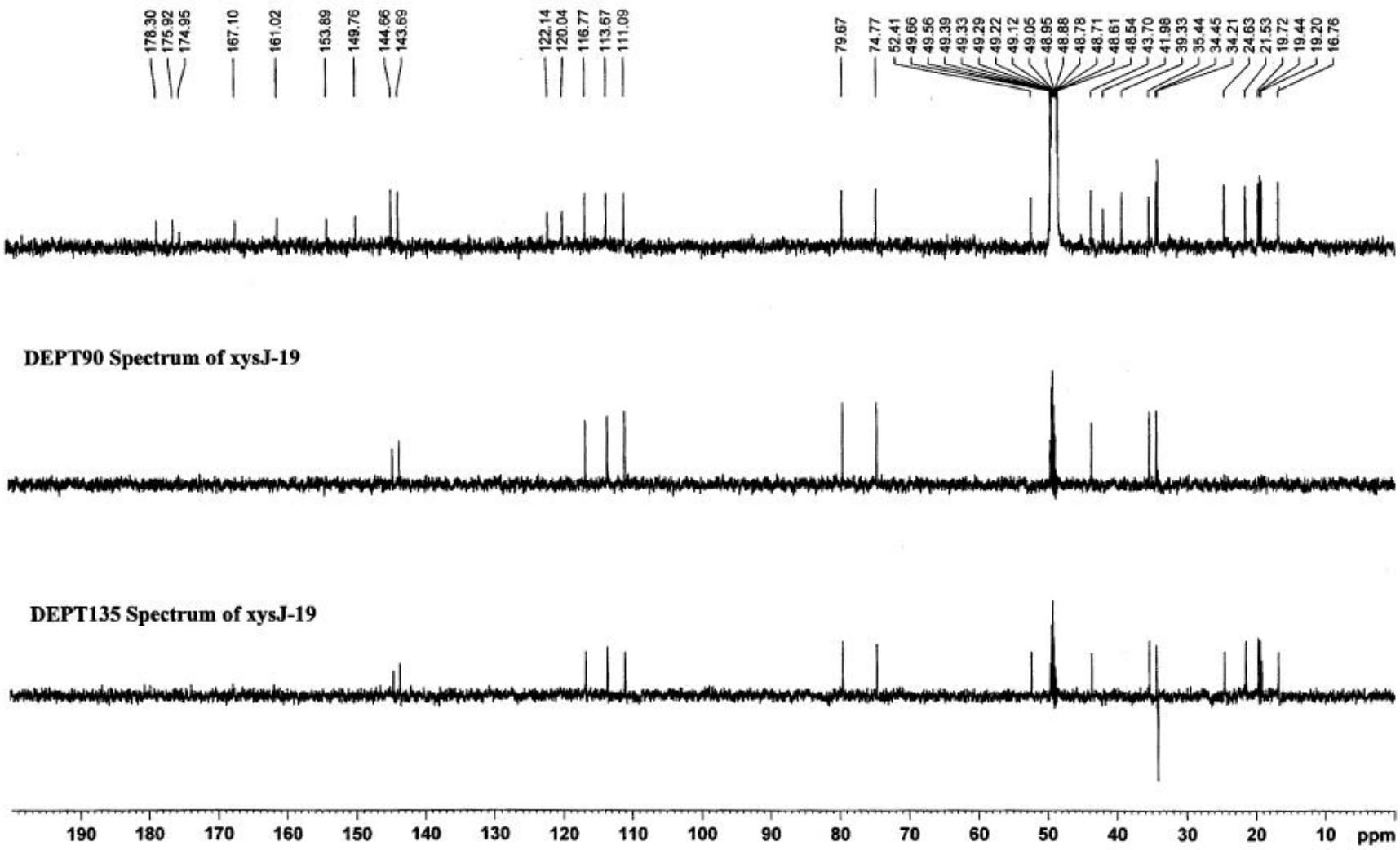
060929_11 136 (2.596) Cn (Cen,4, 80.00, Ar); Sm (SG, 2x3.00); Cm (113:150) TOF MS ES+
1.18e5



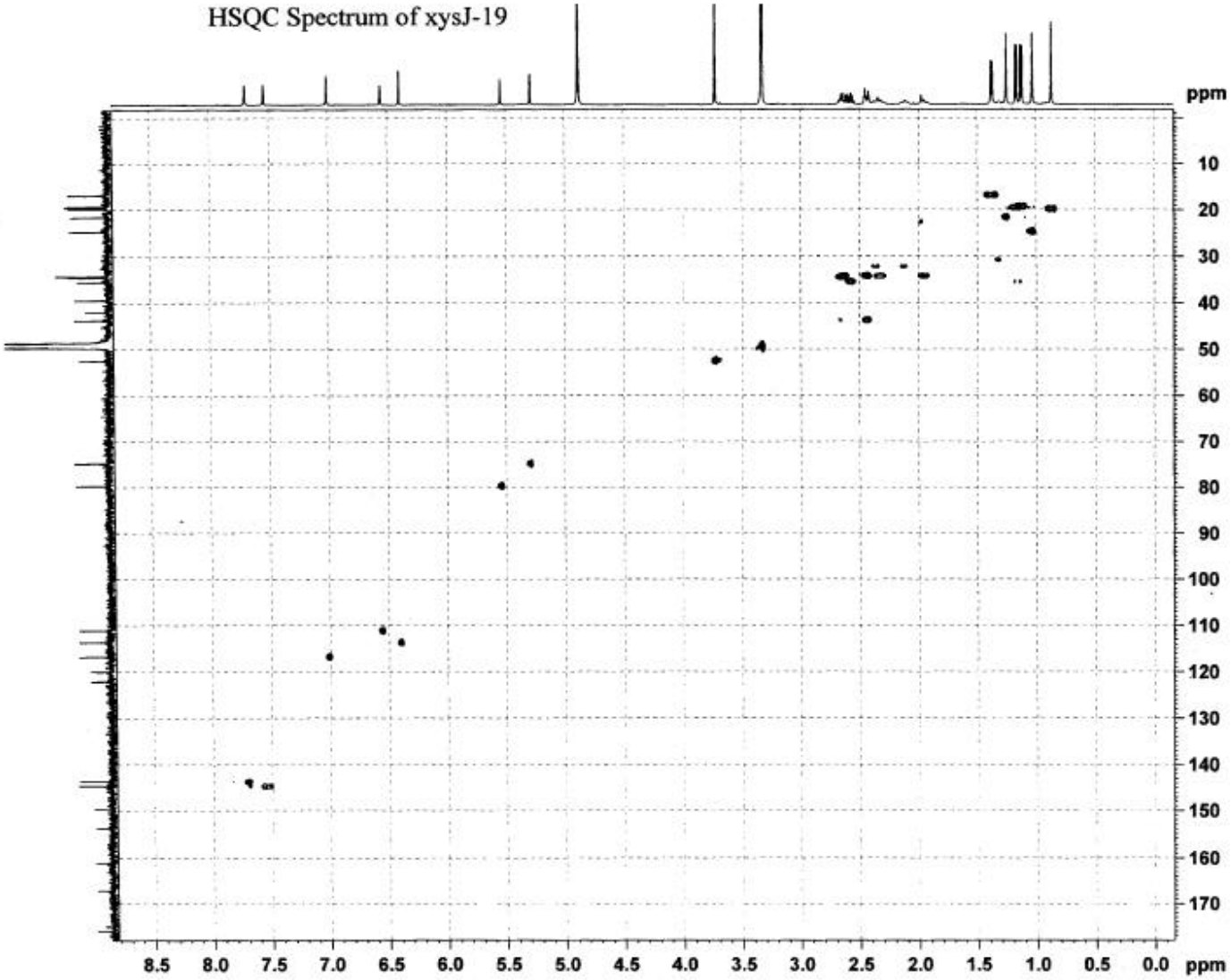
^{1}H NMR (500 MHz) Spectrum of xylogranatin P (**11**) in methanol-d_4



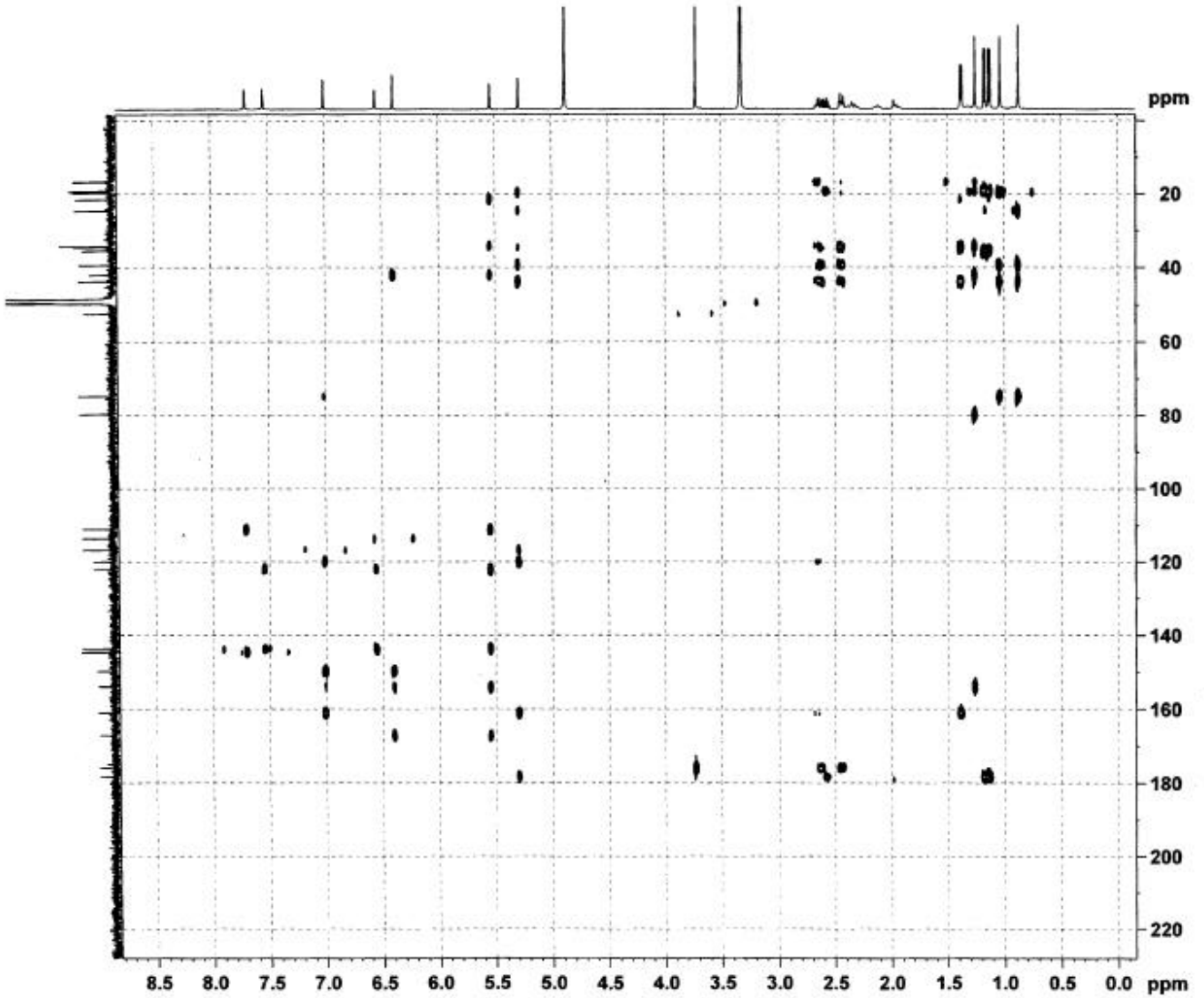
^{13}C NMR (125 MHz) Spectrum and DEPT experiments of xylogranatin P (**11**) in methanol-d_4



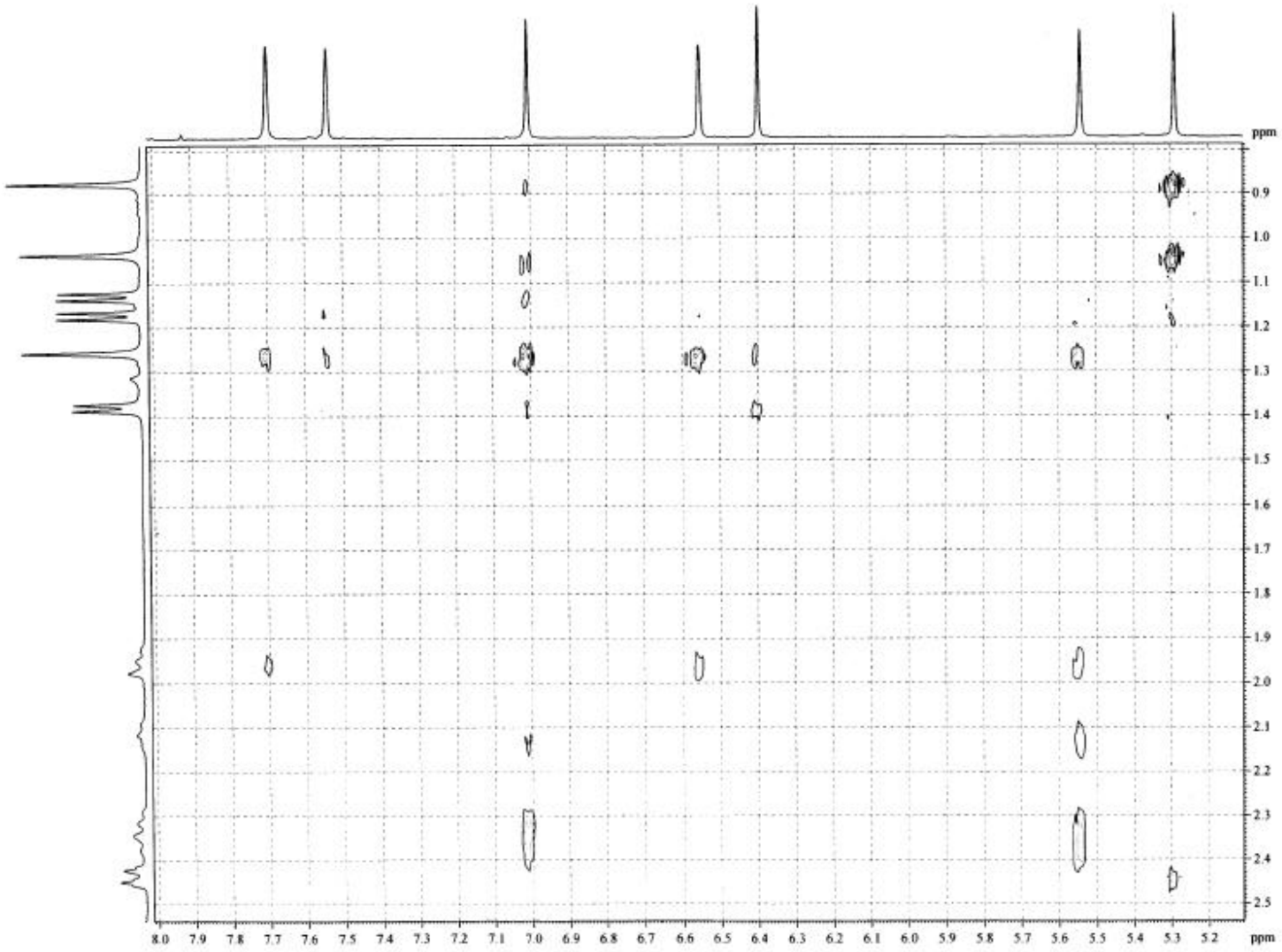
HSQC Spectrum of xylogranatin P (**11**) in methanol-d_4



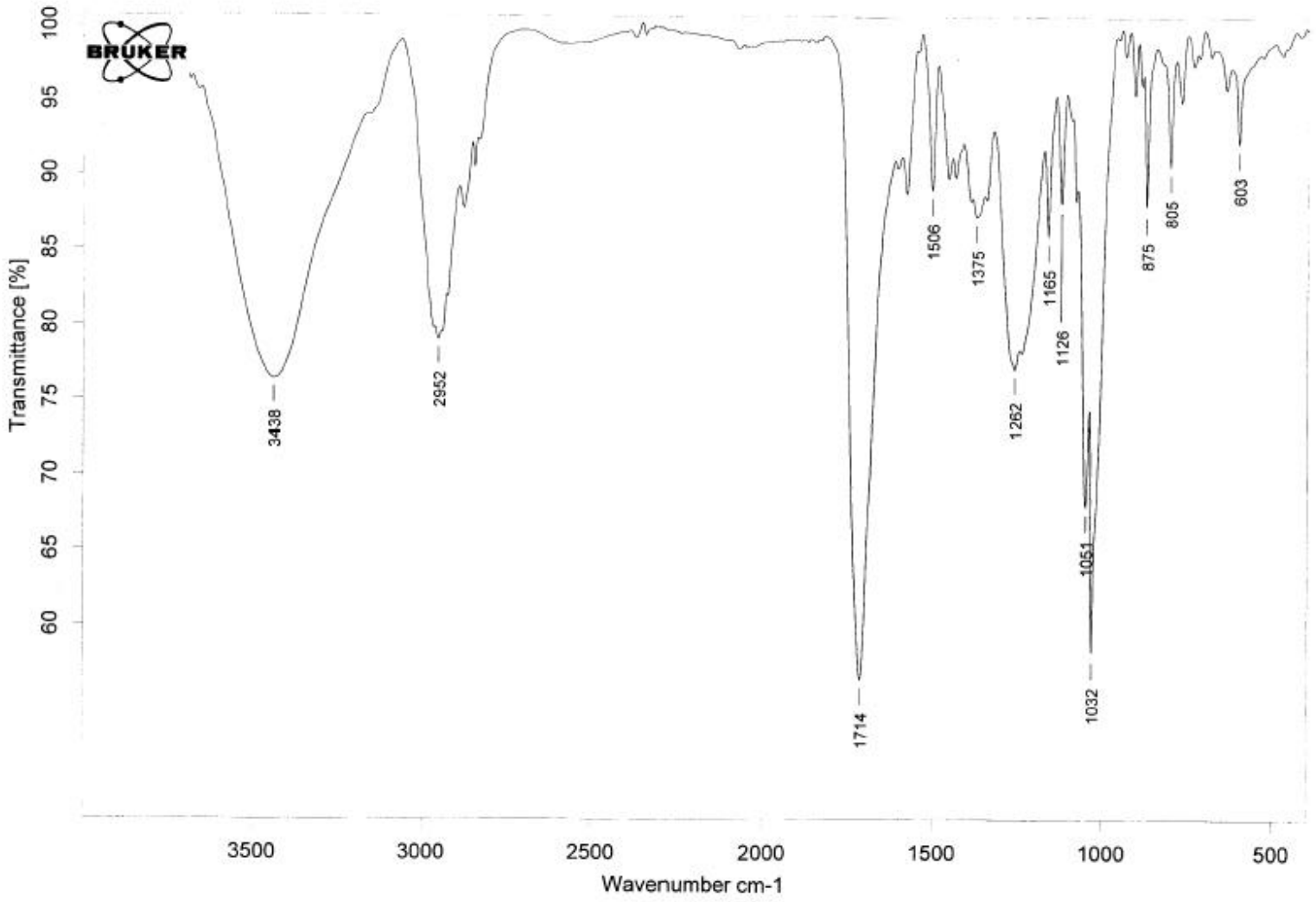
HMBC Spectrum of xylogranatin P (**11**) in methanol-d_4



A Segment of NOESY Spectrum of xylogranatin P (**11**) in methanol-d_4



IR spectrum of xylogranatin Q (**12**)



HR-TOFMS of xylogranatin Q (**12**)

Elemental Composition Report

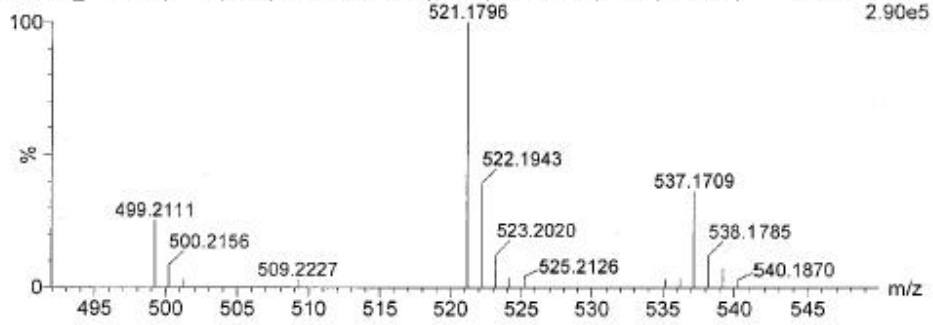
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
58 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

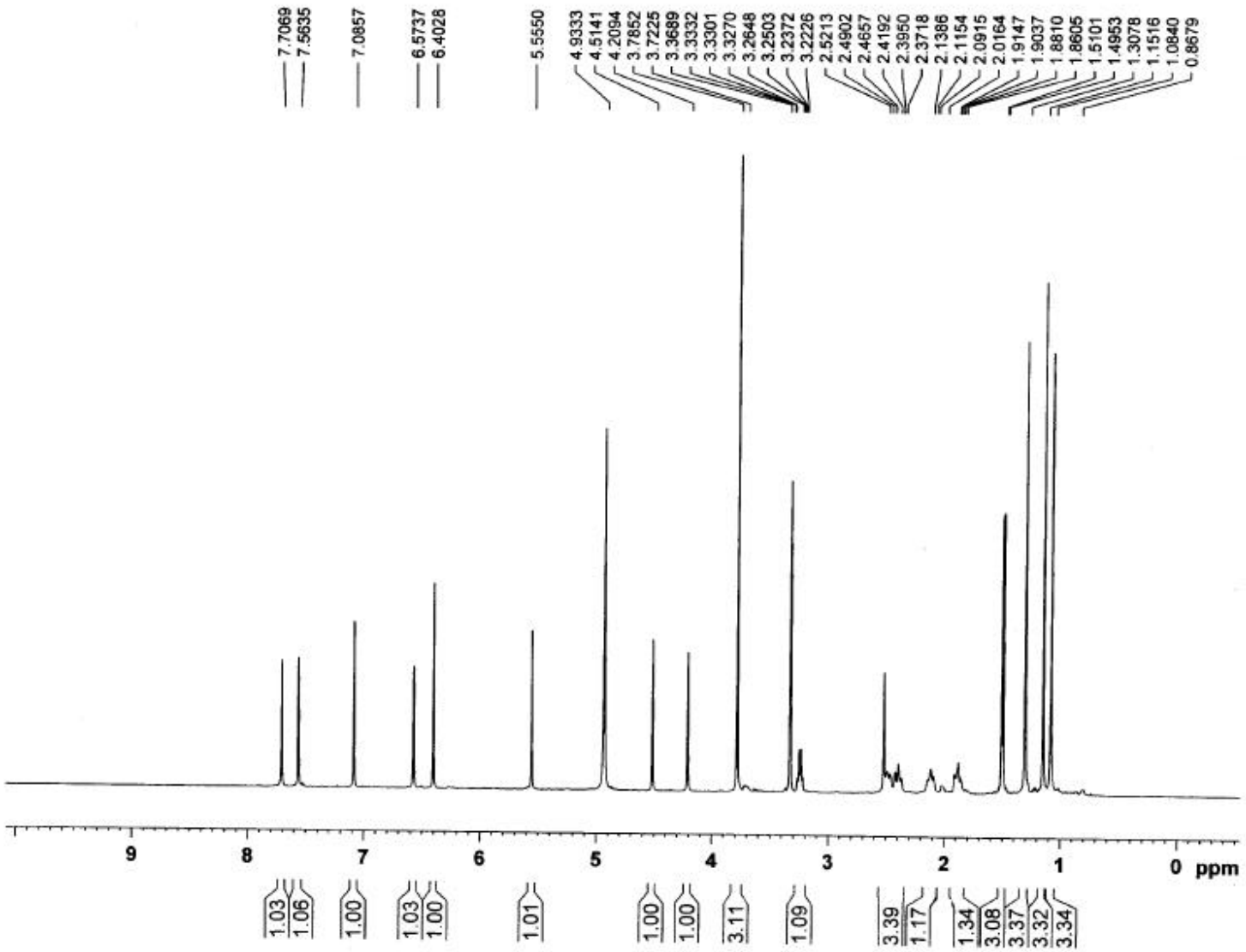
Minimum:				-1.5		
Maximum:		200.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
521.1796	521.1788	0.8	1.6	12.5	2	C27 H30 O9 23Na
	521.1812	-1.6	-3.0	15.5	1	C29 H29 O9

Wu06

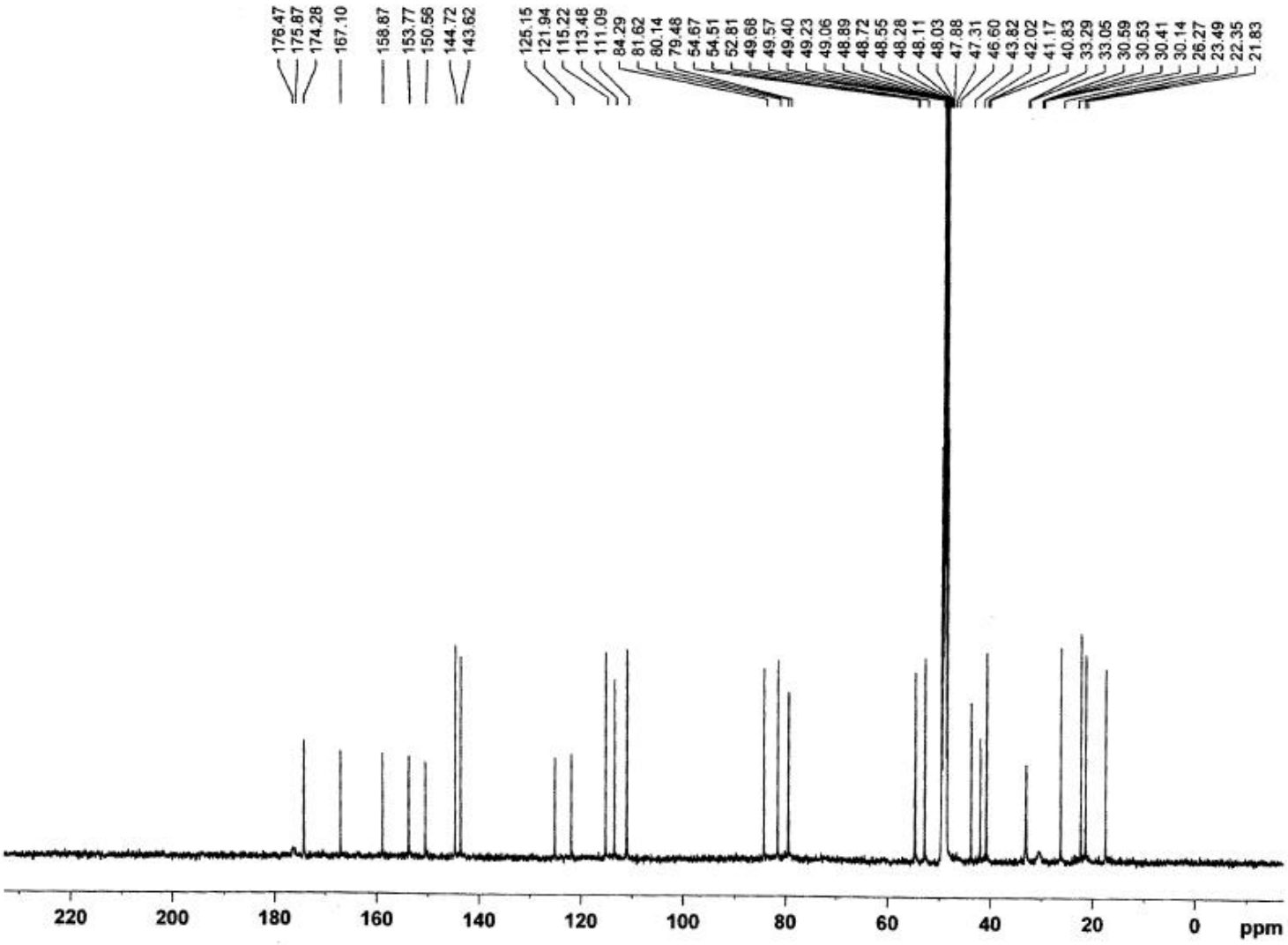
060929_09 163 (3.099) Cn (Cen,4, 80.00, Ar); Sm (SG, 2x3.00); Cm (139:164) TOF MS ES+ 2.90e5



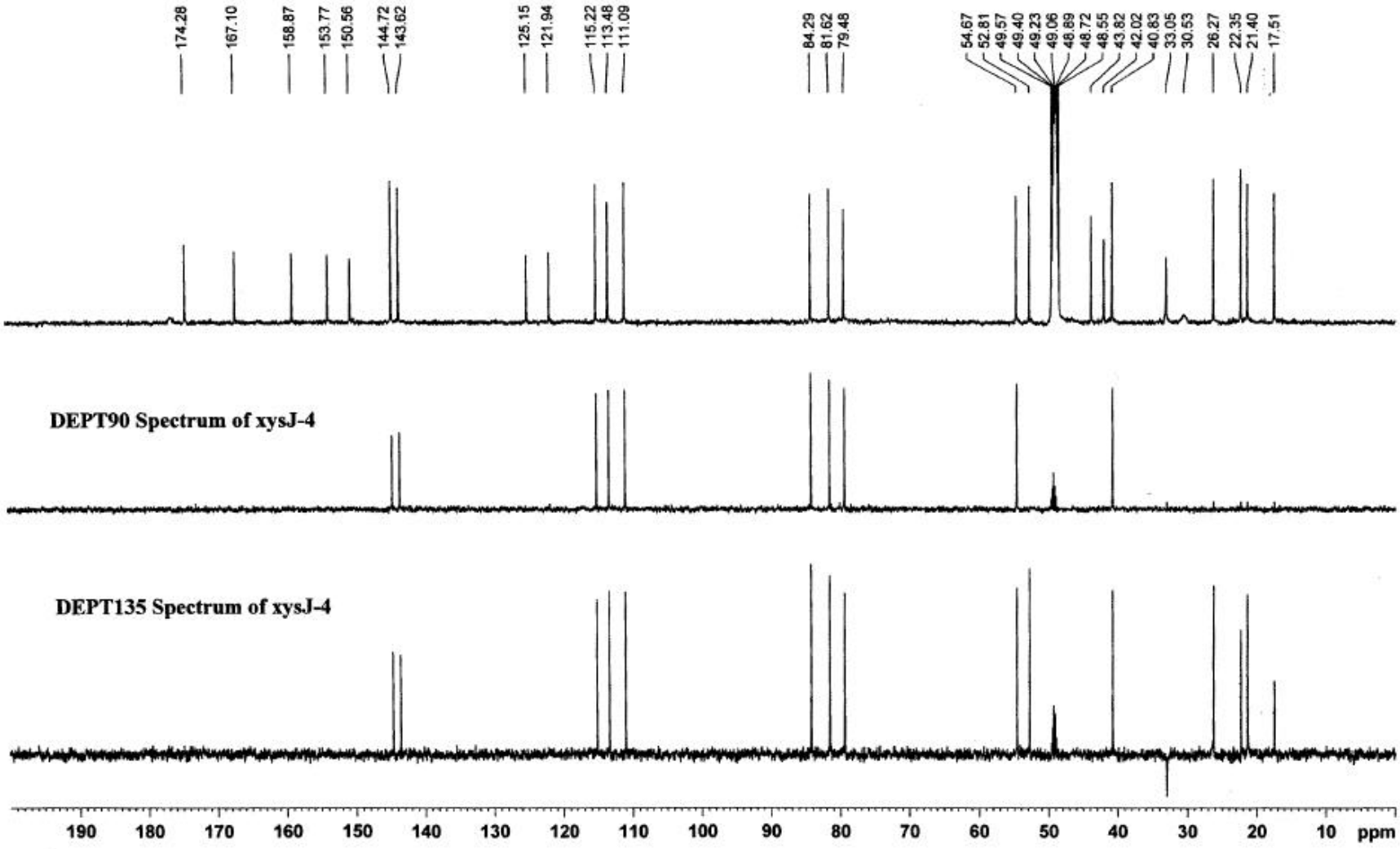
^{1}H NMR (500 MHz) Spectrum of xylogranatin Q (**12**) in methanol-d_4



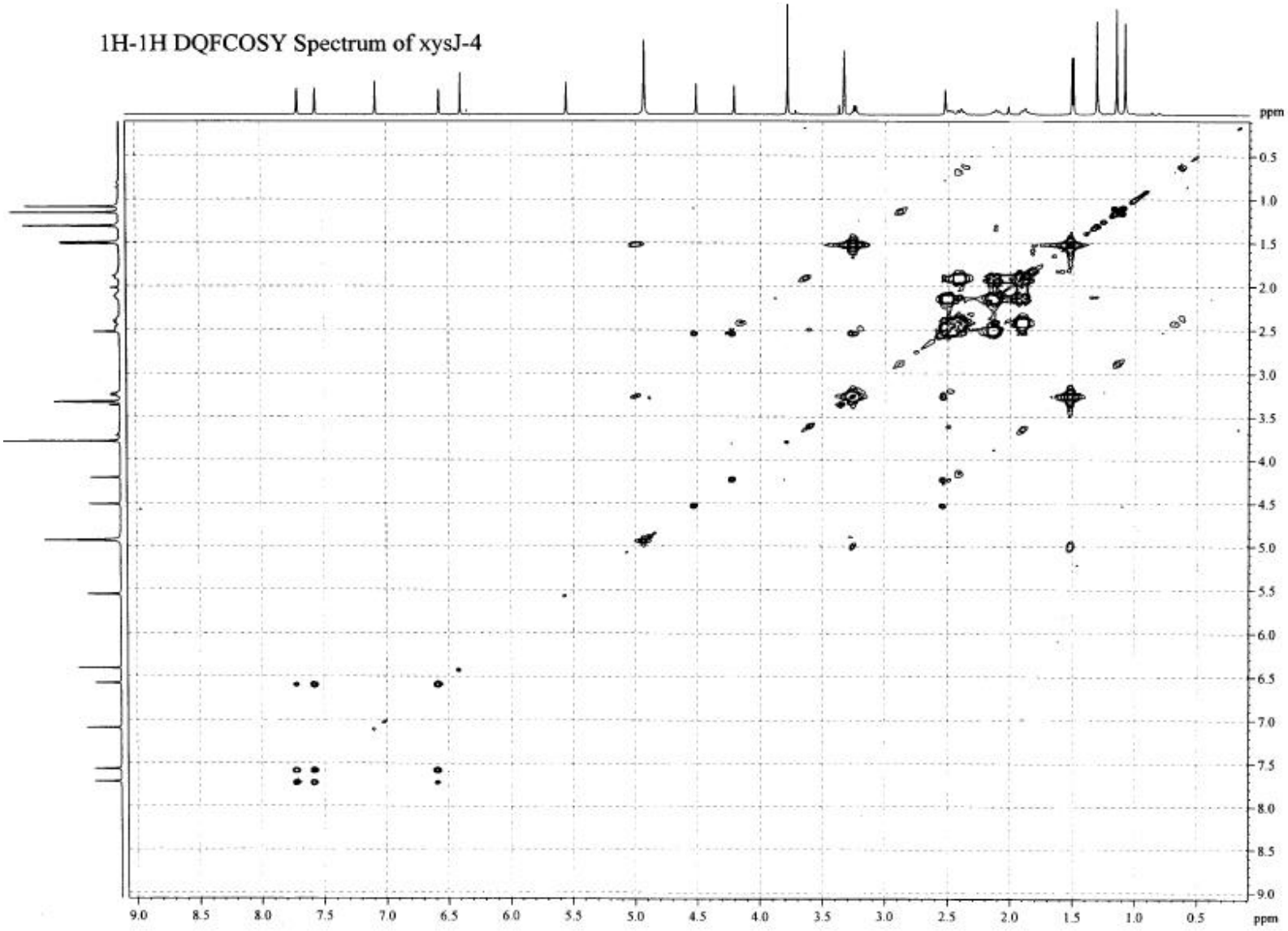
^{13}C NMR (125 MHz) Spectrum of xylogranatin Q (**12**) in methanol-d_4



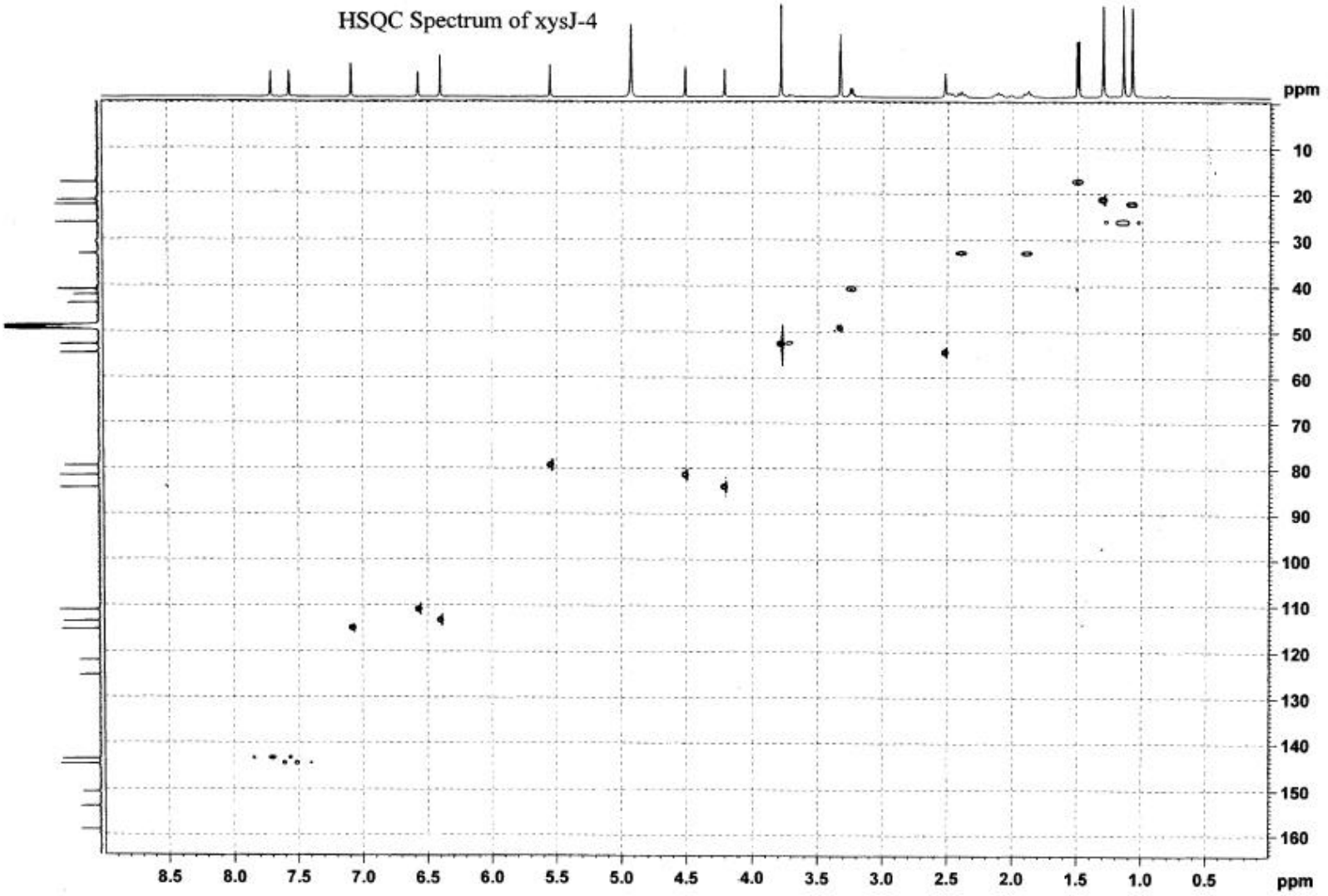
DEPT experiments of xylogranatin Q (**12**) in methanol-d_4



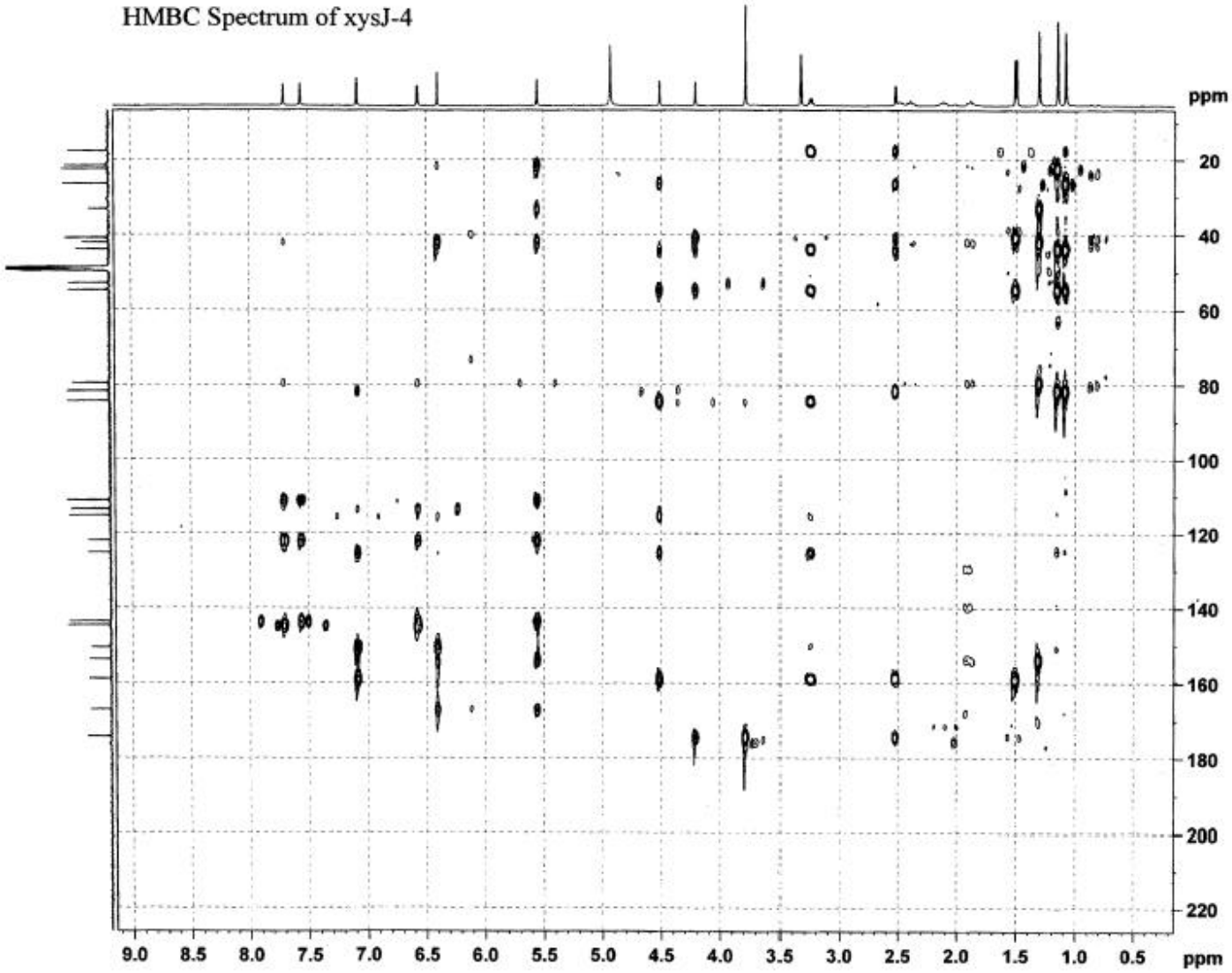
^{1}H-^{1}H COSY Spectrum of xylogranatin Q (**12**) in methanol-d_4



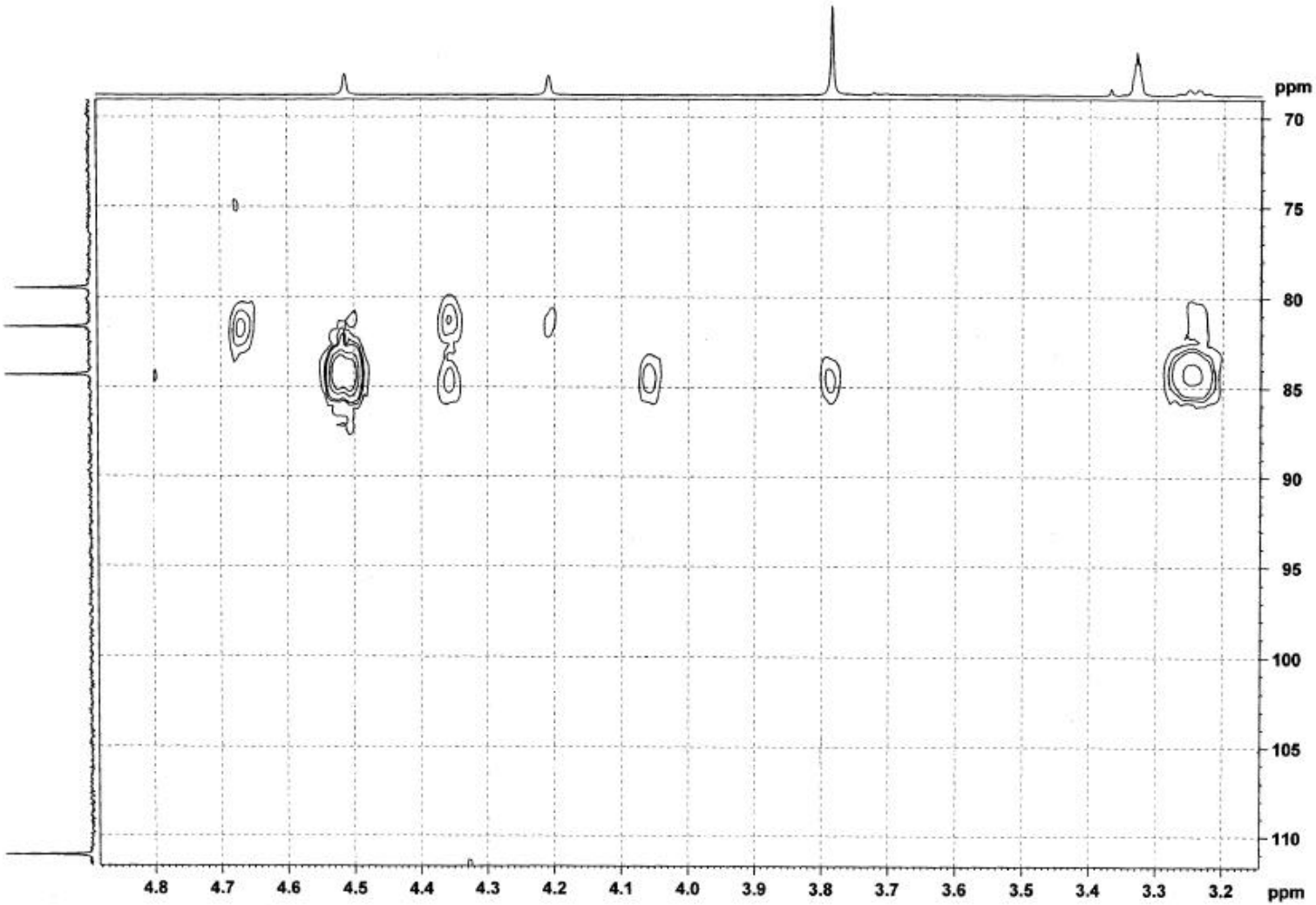
HSQC Spectrum of xylogranatin Q (**12**) in methanol-d_4



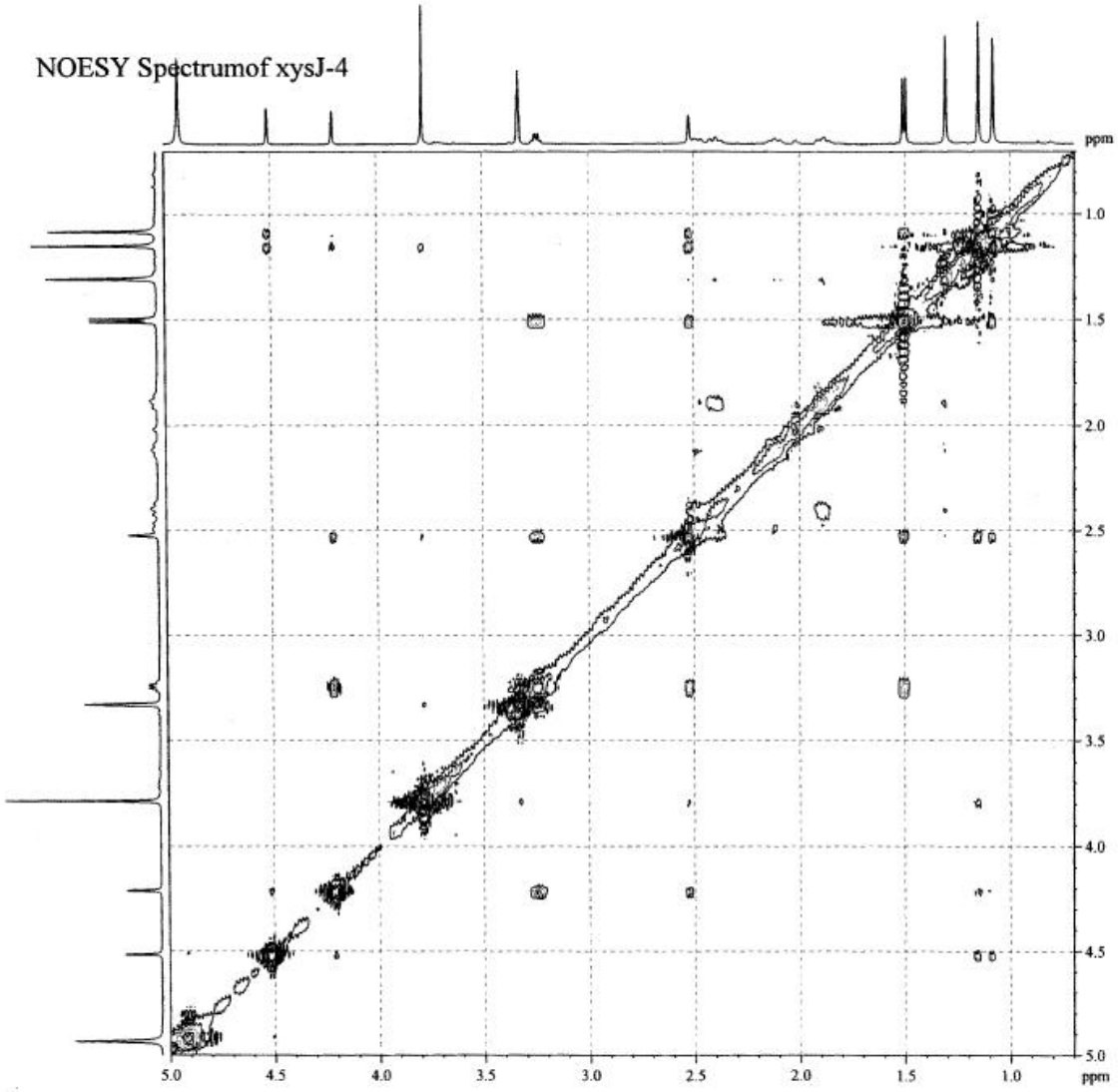
HMBC Spectrum of xylogranatin Q (**12**) in methanol-d_4



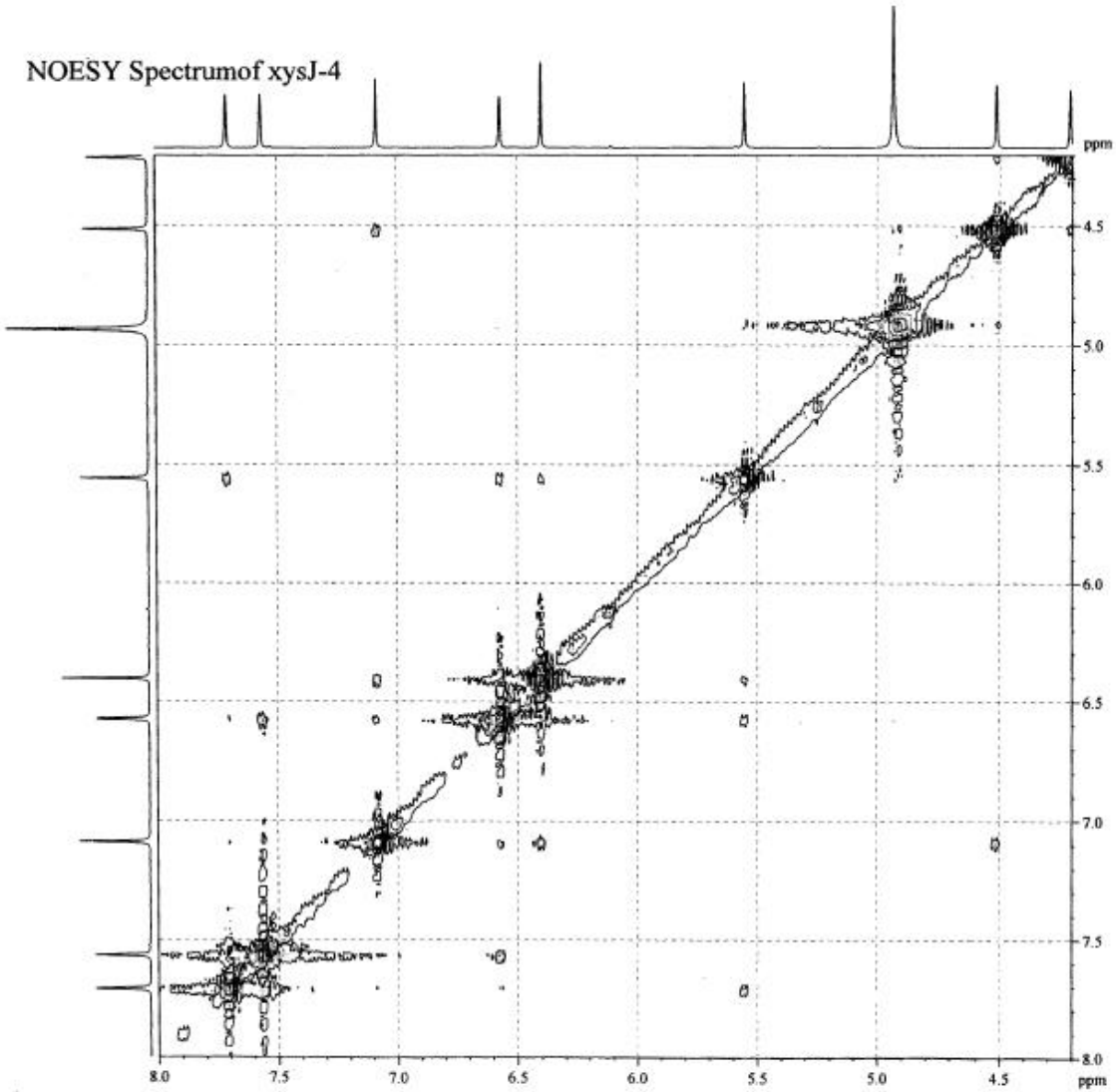
A Segment of HMBC Spectrum of xylogranatin Q (**12**) in methanol-d_4



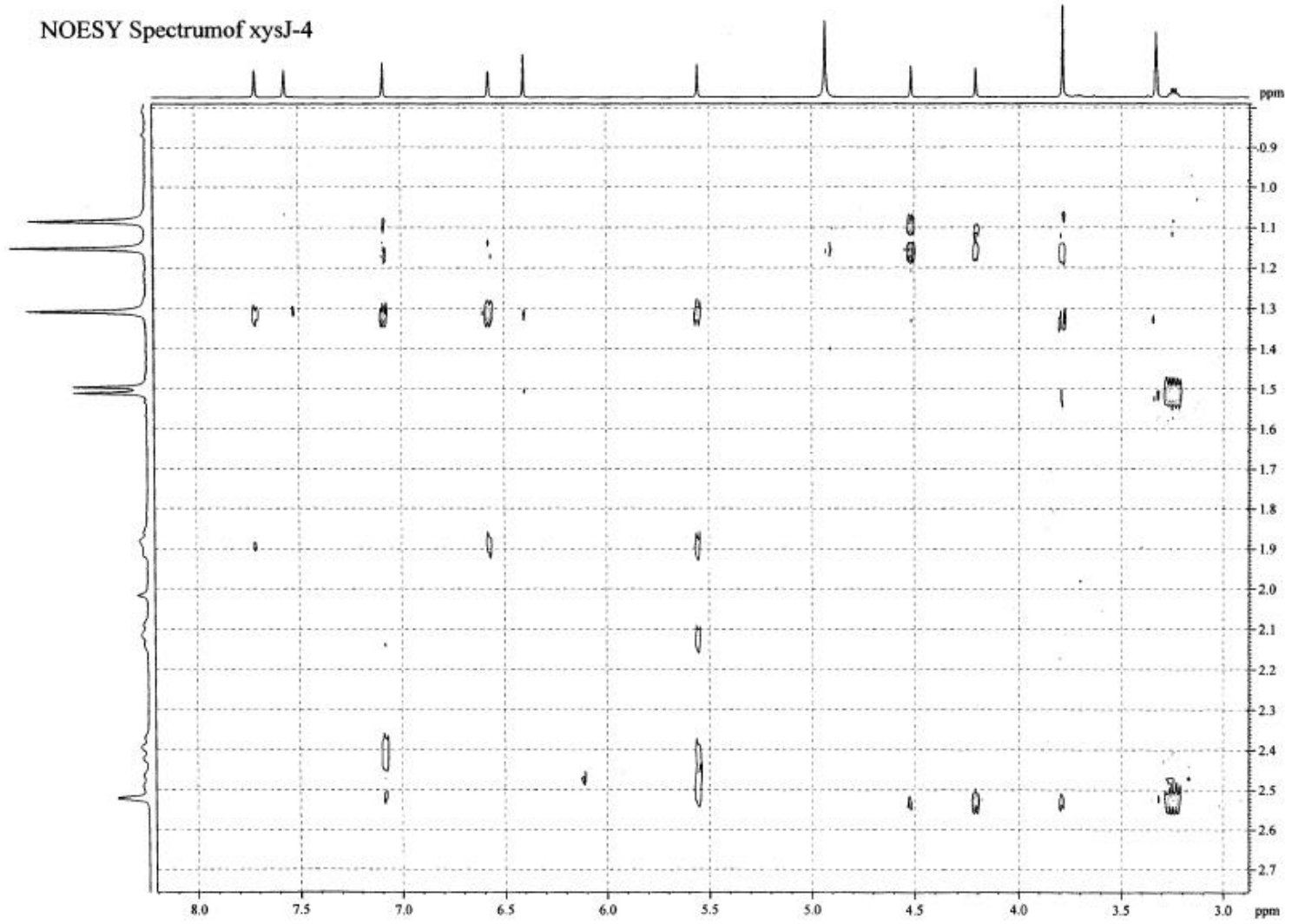
A Segment of NOESY Spectrum of xylogranatin Q (**12**) in methanol-d_4



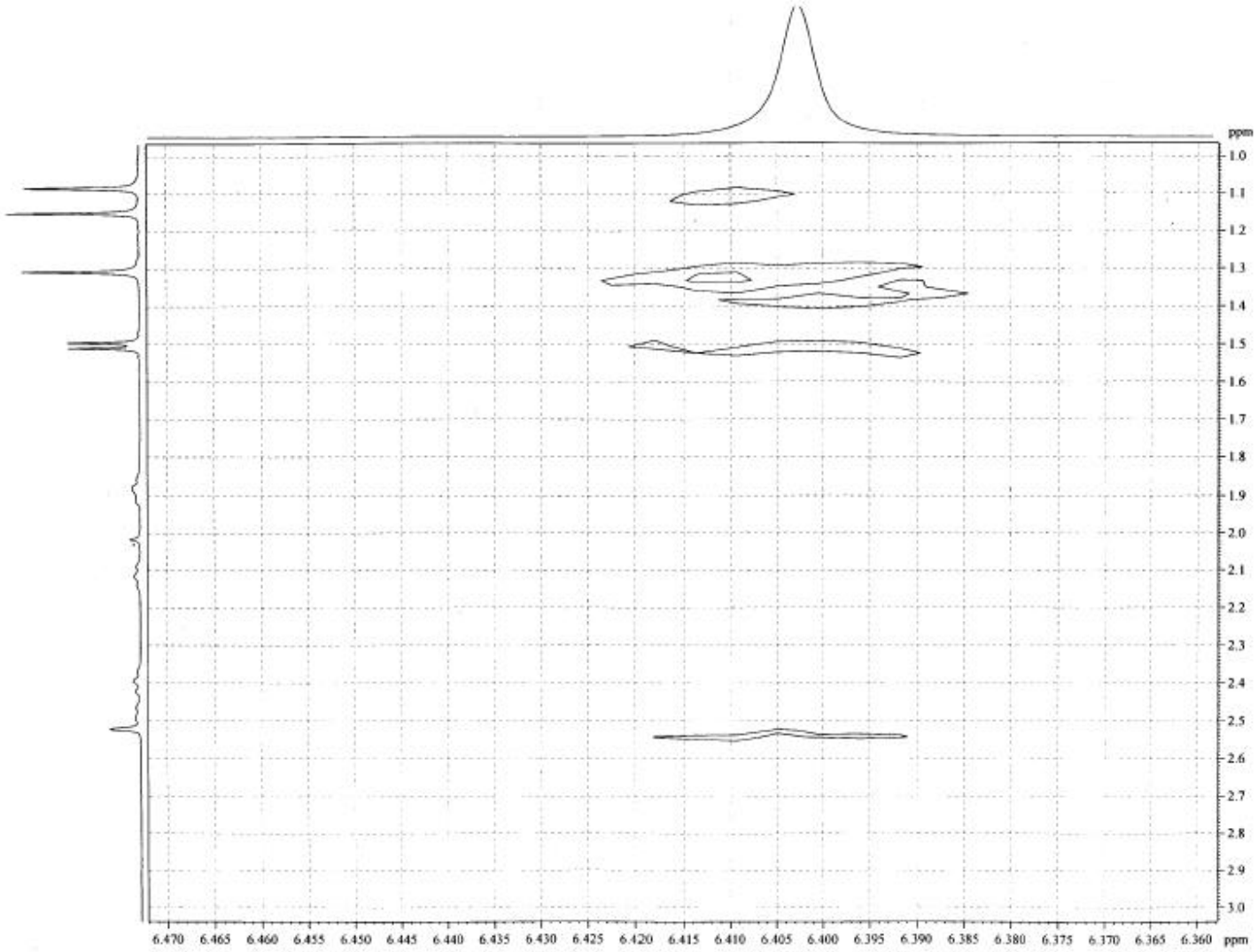
A Segment of NOESY Spectrum of xylogranatin Q (**12**) in methanol-d_4



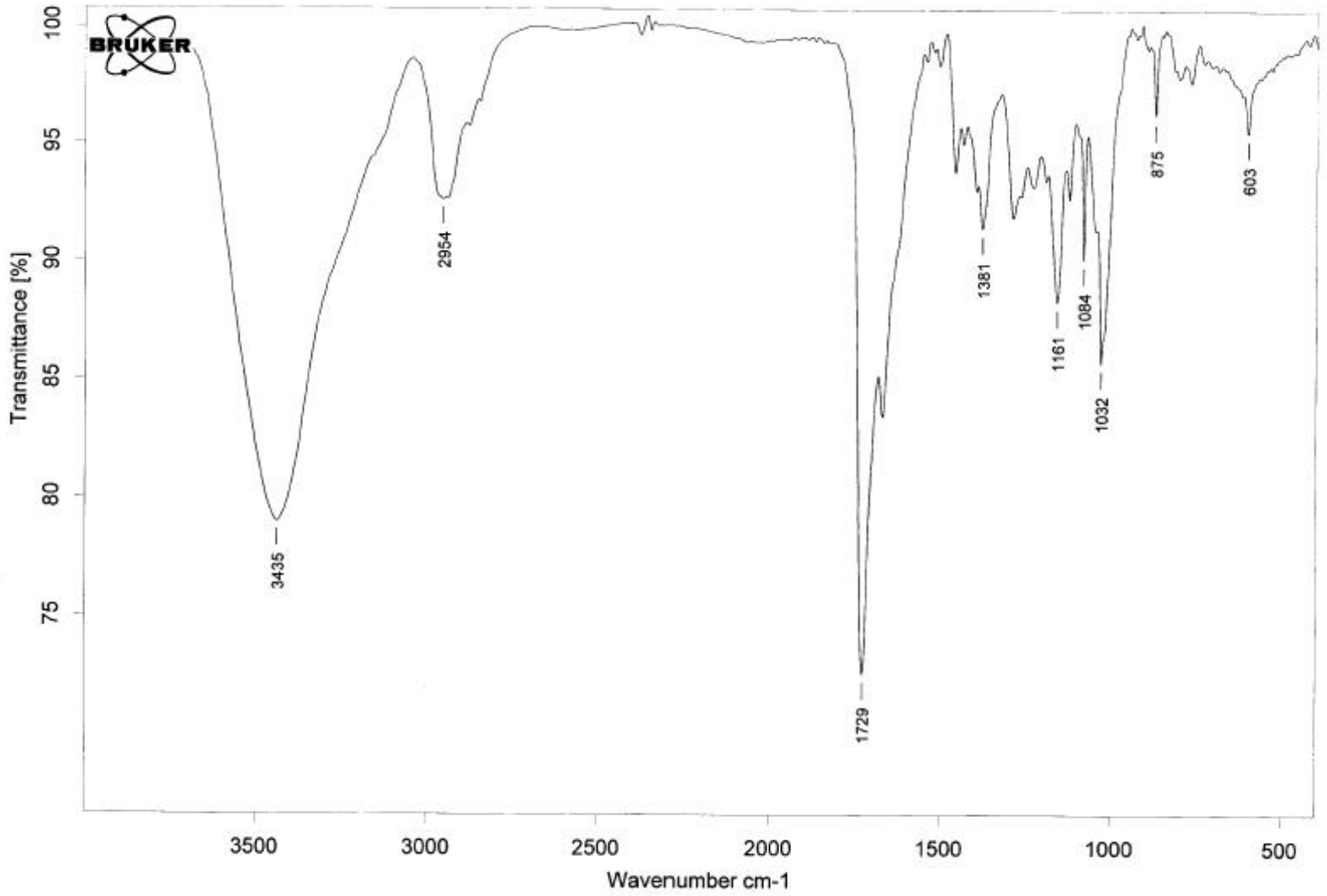
A Segment of NOESY Spectrum of xylogranatin Q (**12**) in methanol-d_4



A Segment of NOESY Spectrum of xylogranatin Q (**12**) in methanol-d_4



IR spectrum of xylogranatin R (**13**)



HR-TOFMS of xylogranatin R (**13**)

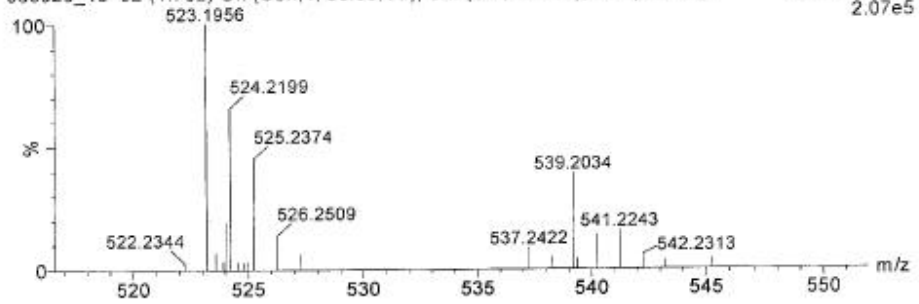
Elemental Composition Report

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

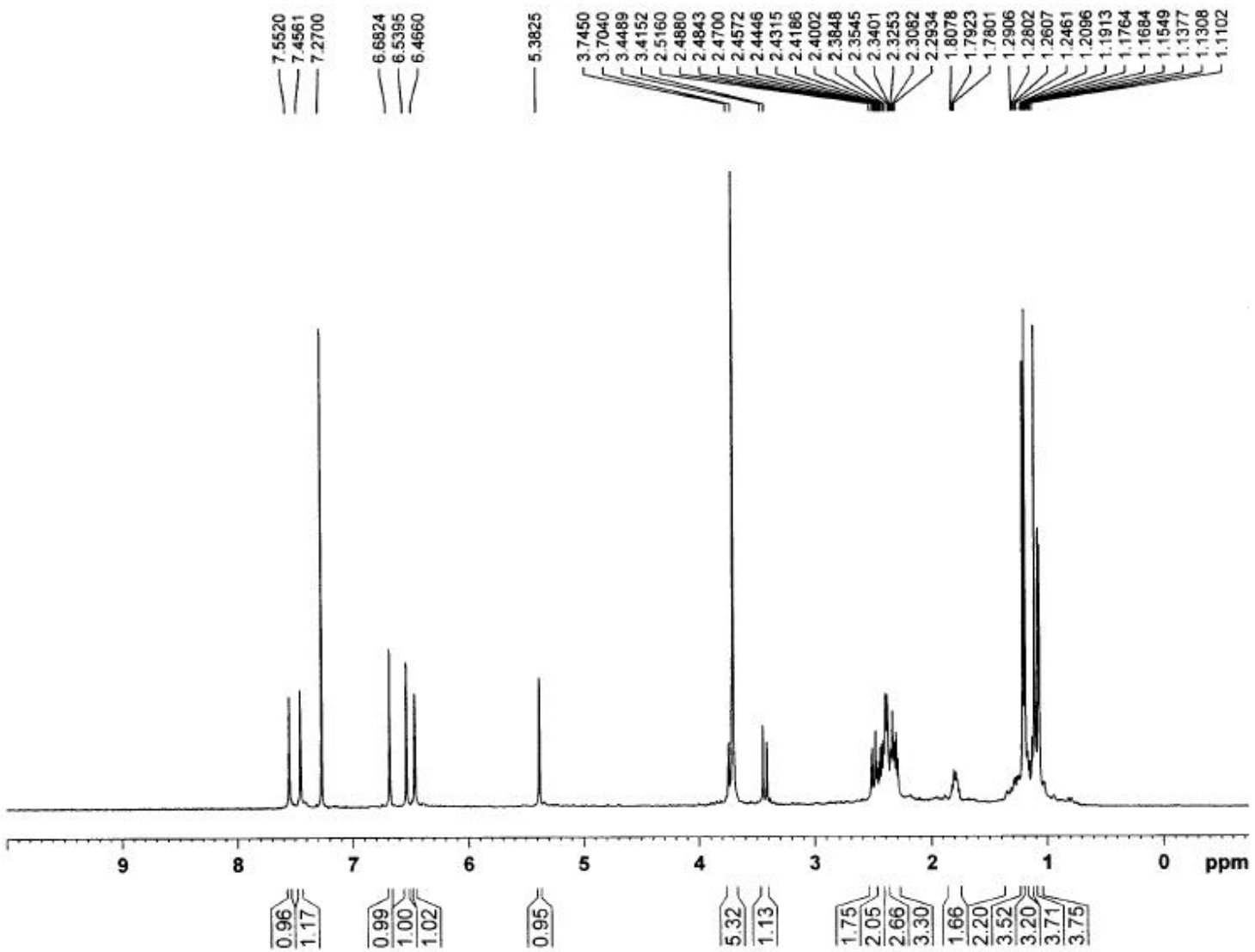
Monoisotopic Mass, Odd and Even Electron Ions
63 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

Minimum:				-1.5		
Maximum:		200.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
523.1956	523.1944	1.2	2.3	11.5	2	C27 H32 O9 23Na
	523.1968	-1.2	-2.3	14.5	1	C29 H31 O9

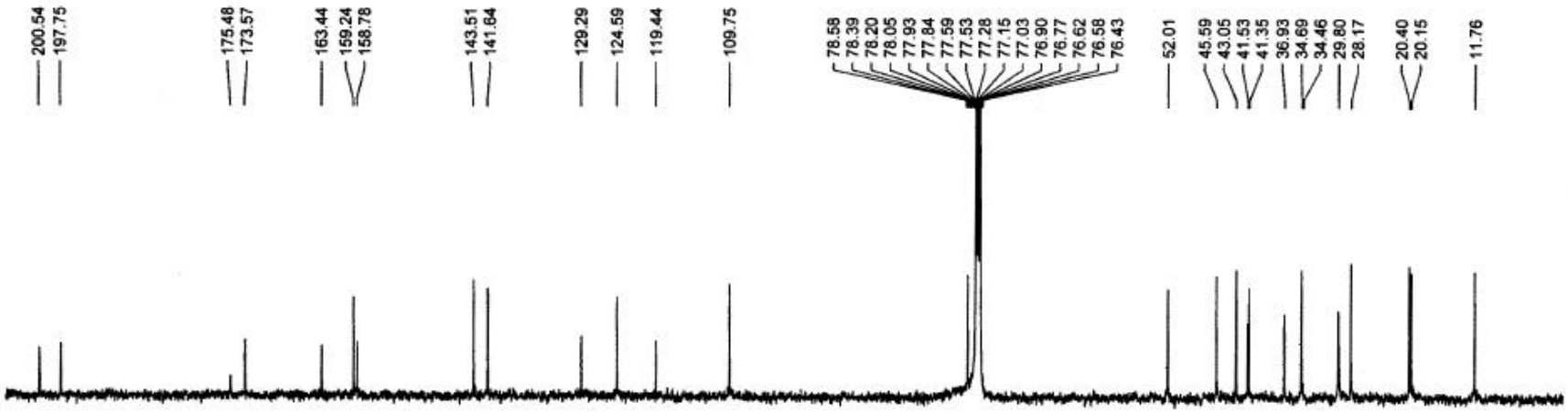
Wu11
060929_13 92 (1.762) Cn (Cen,4, 80.00, Ar); Sm (SG, 2x3.00); Cm (92:114) TOF MS ES+
2.07e5



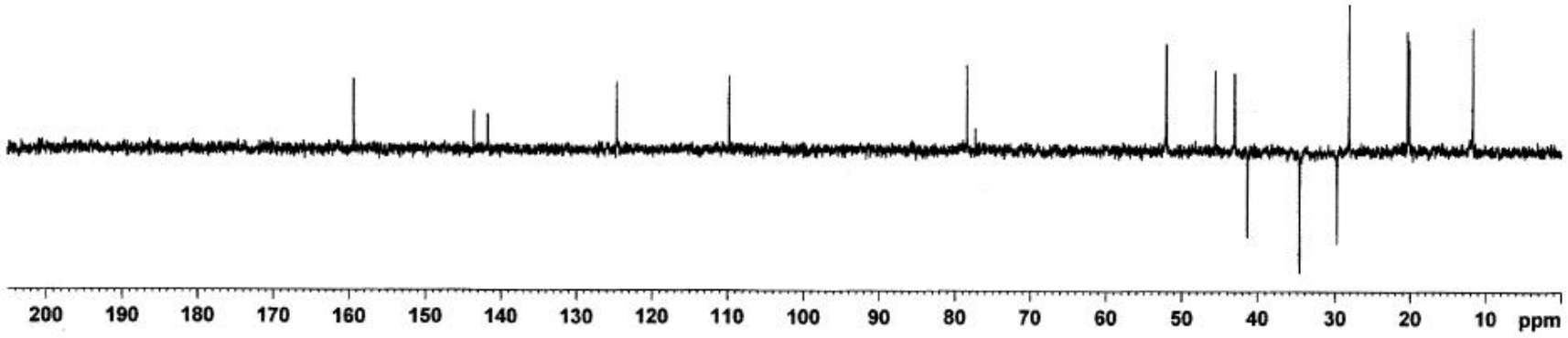
^{1}H NMR (500 MHz) Spectrum of xylogranatin R (**13**) in $CDCl_3$



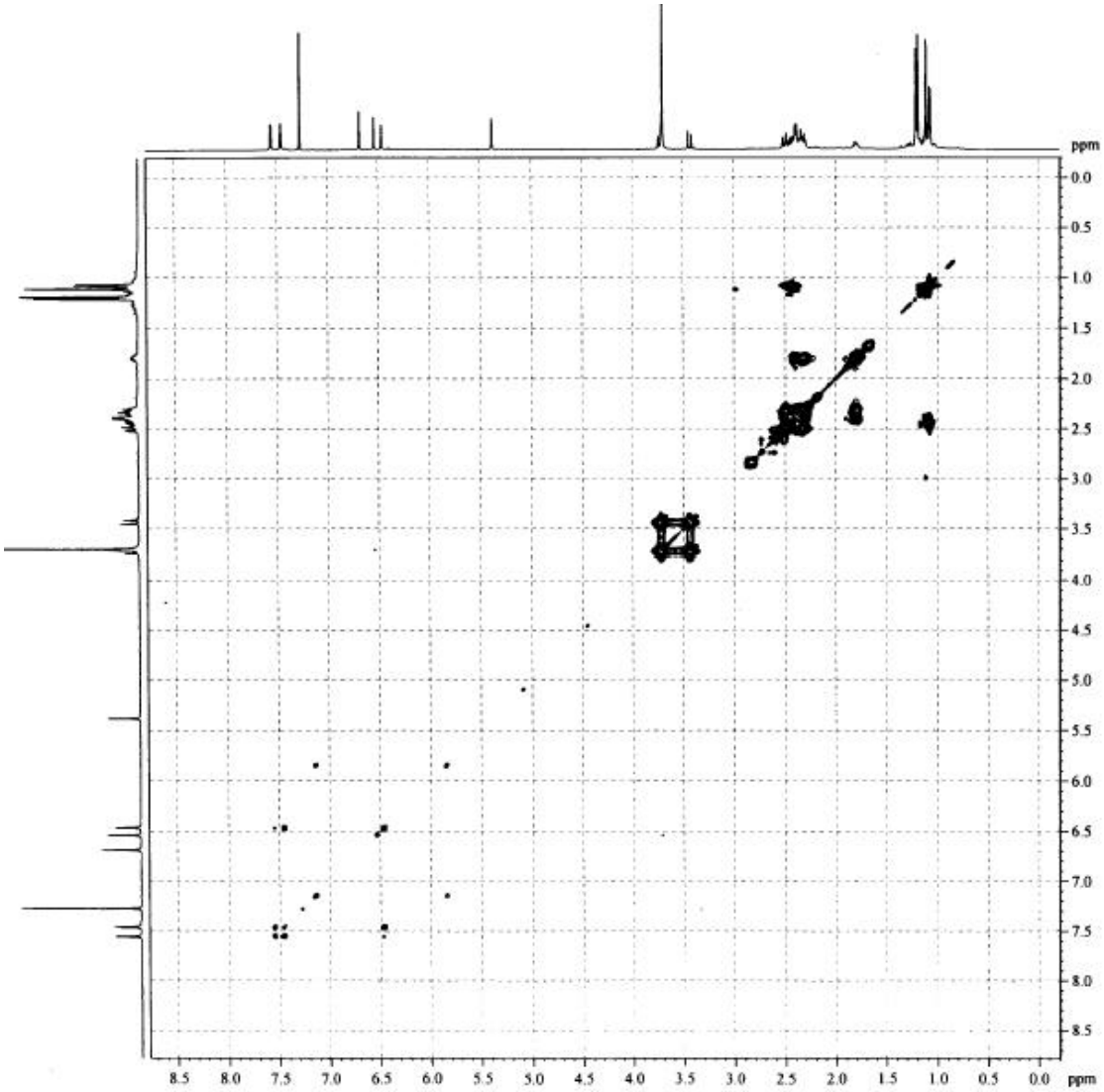
^{13}C NMR (125 MHz) Spectrum and DEPT experiments of xylogranatin R (**13**) in $CDCl_3$



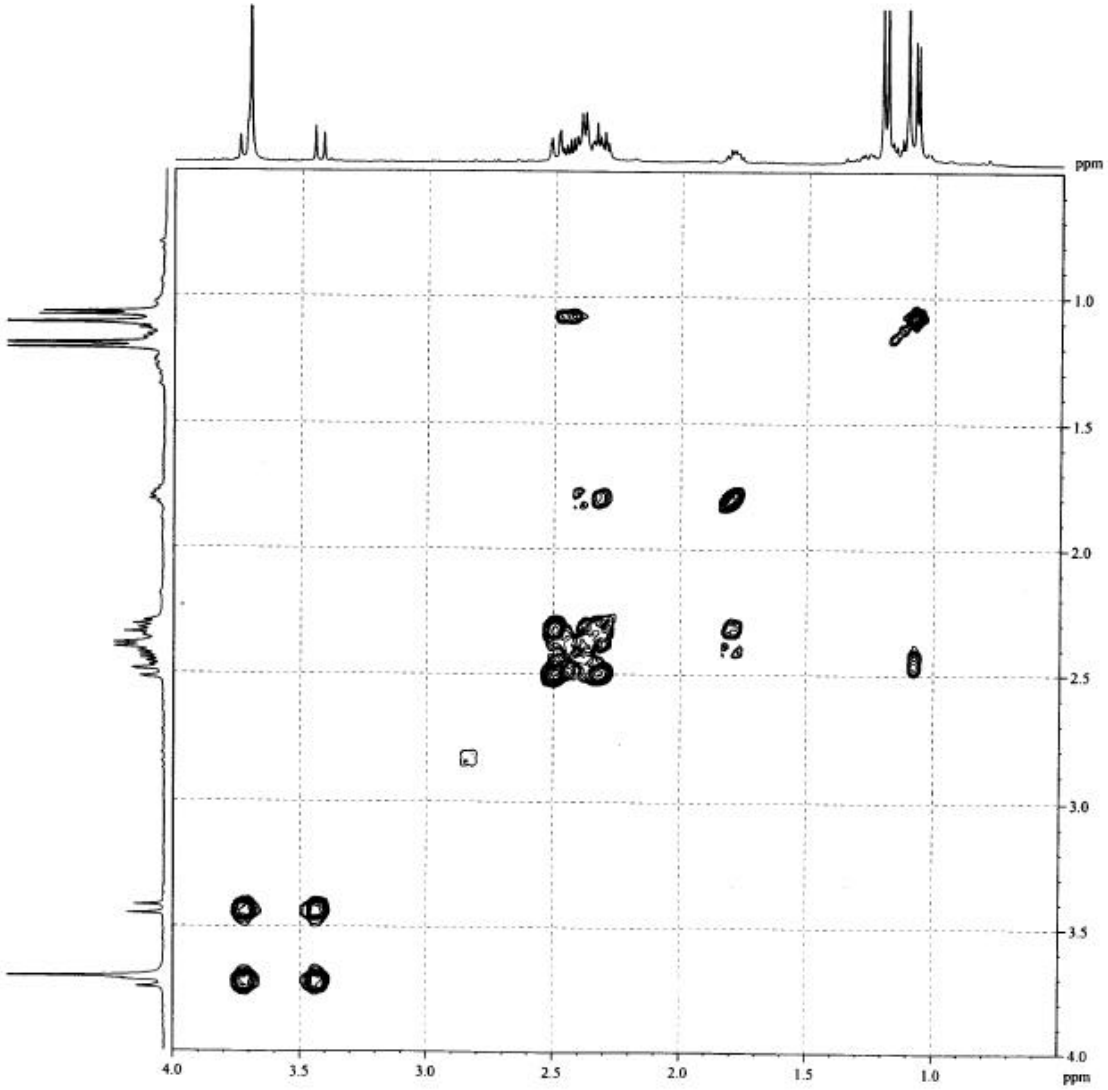
DEPT135 Spectrum of xysJ-5



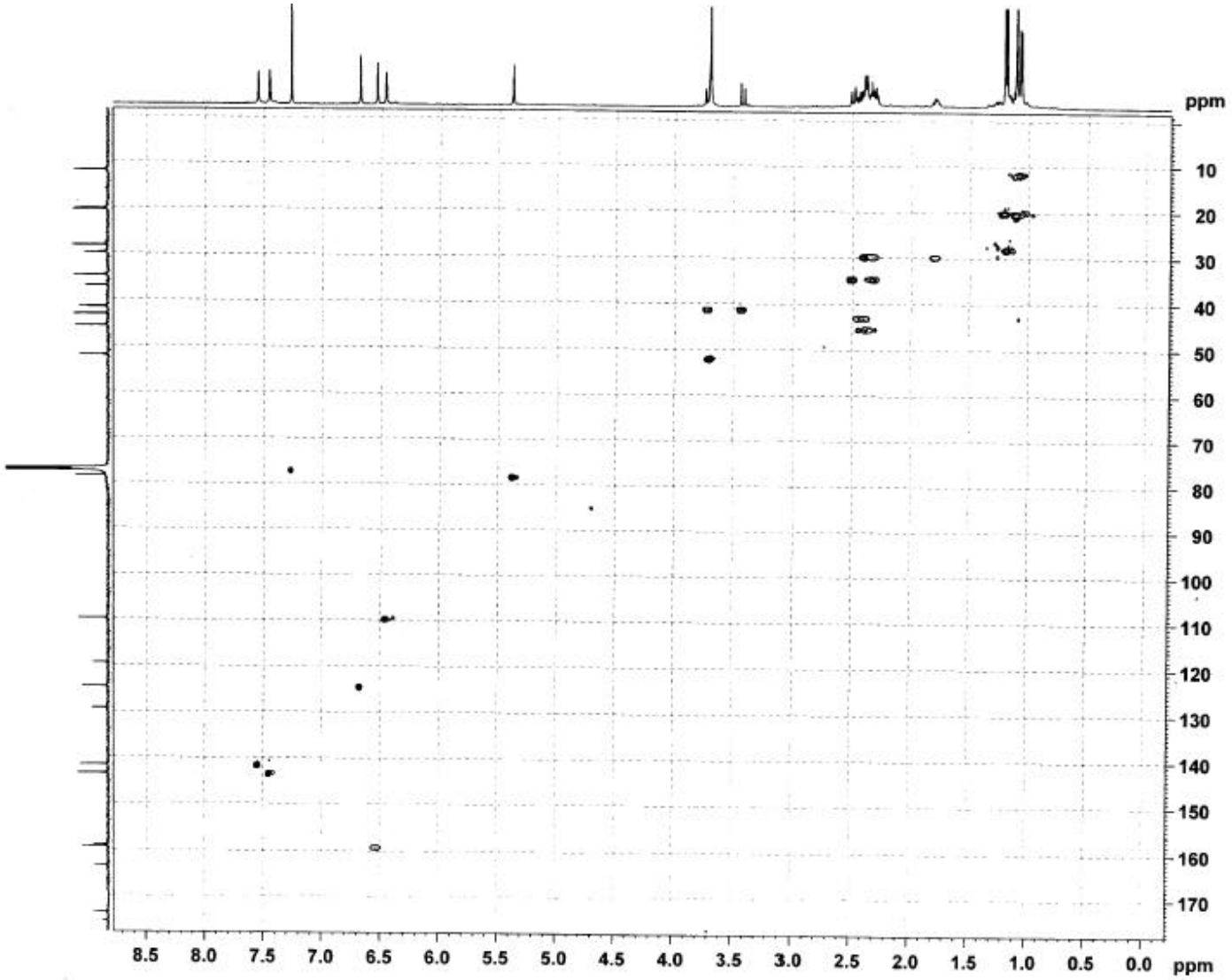
^{1}H-^{1}H COSY Spectrum of xylogranatin R (**13**) in $CDCl_3$



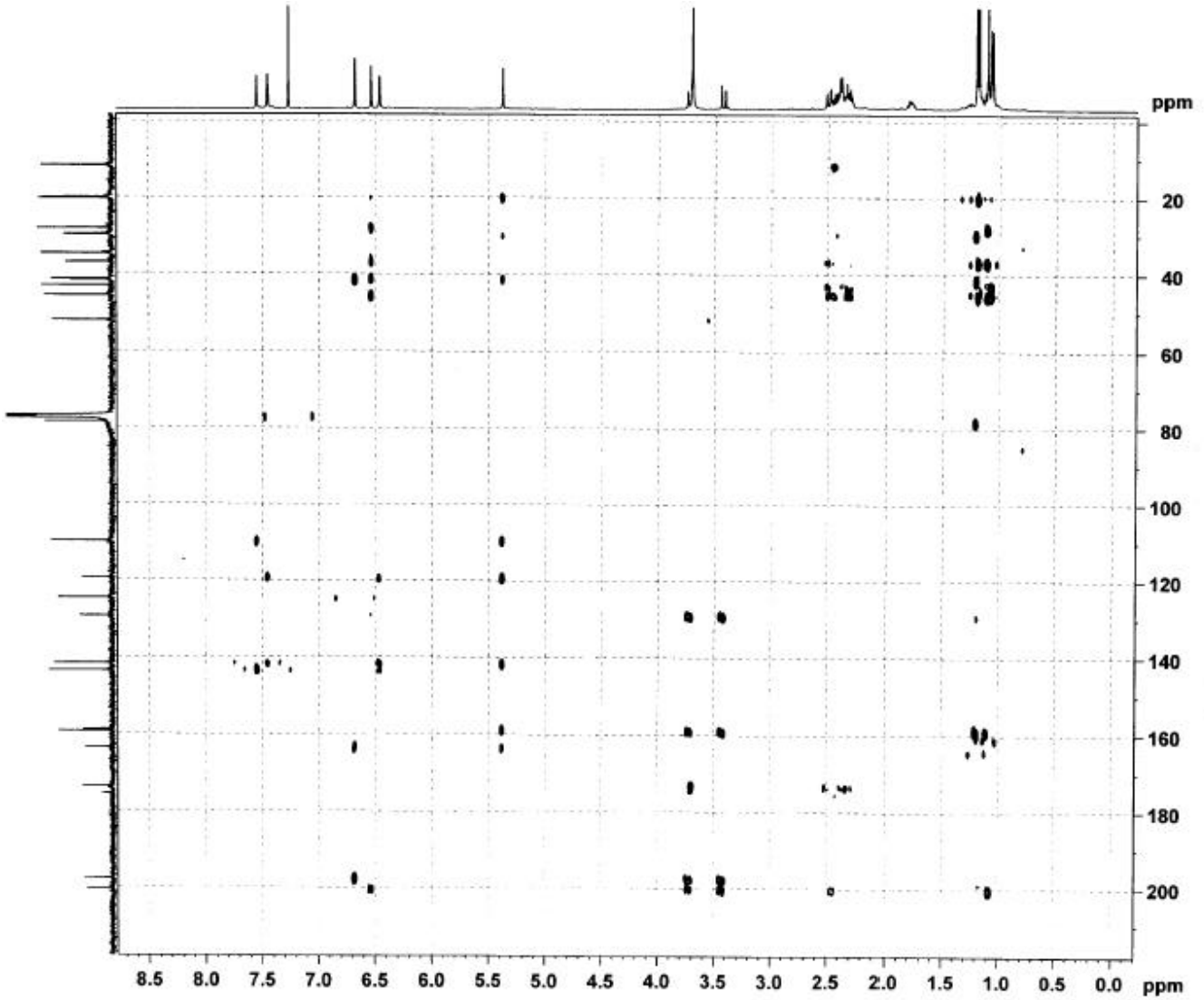
A Segment of ^{1}H-^{1}H COSY Spectrum of xylogranatin R (**13**) in $CDCl_3$



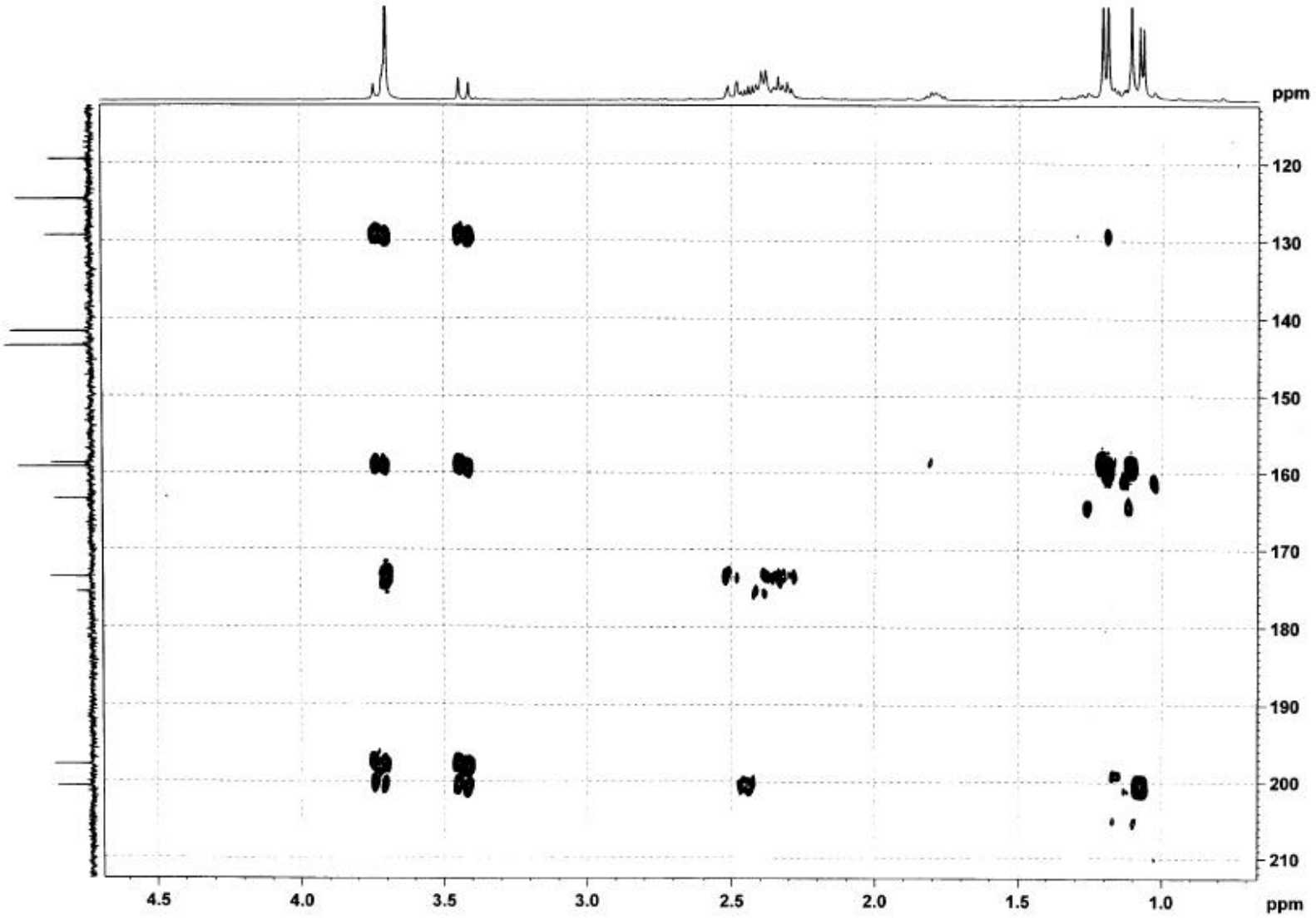
HSQC Spectrum of xylogranatin R (**13**) in $CDCl_3$



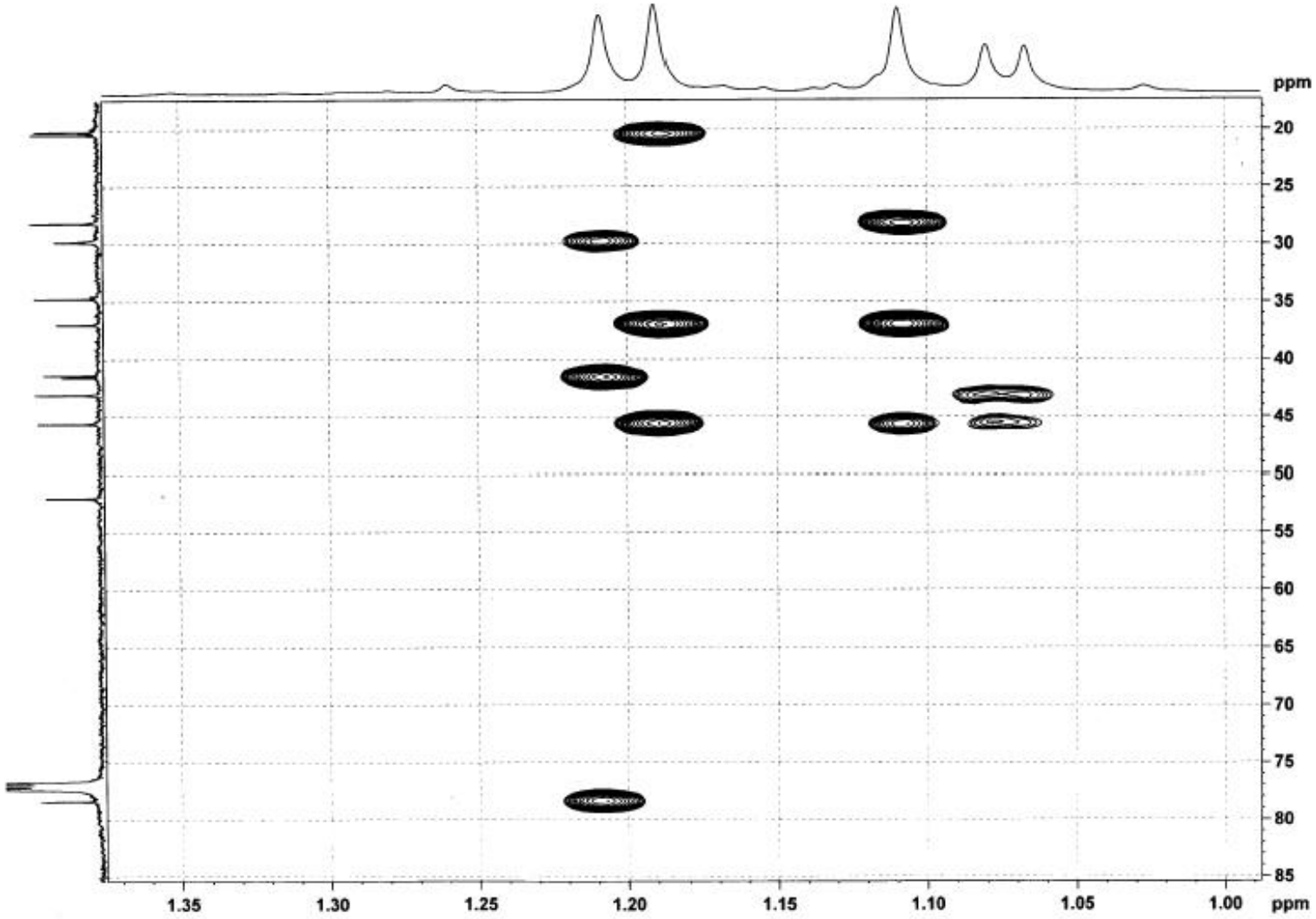
HMBC Spectrum of xylogranatin R (**13**) in $CDCl_3$



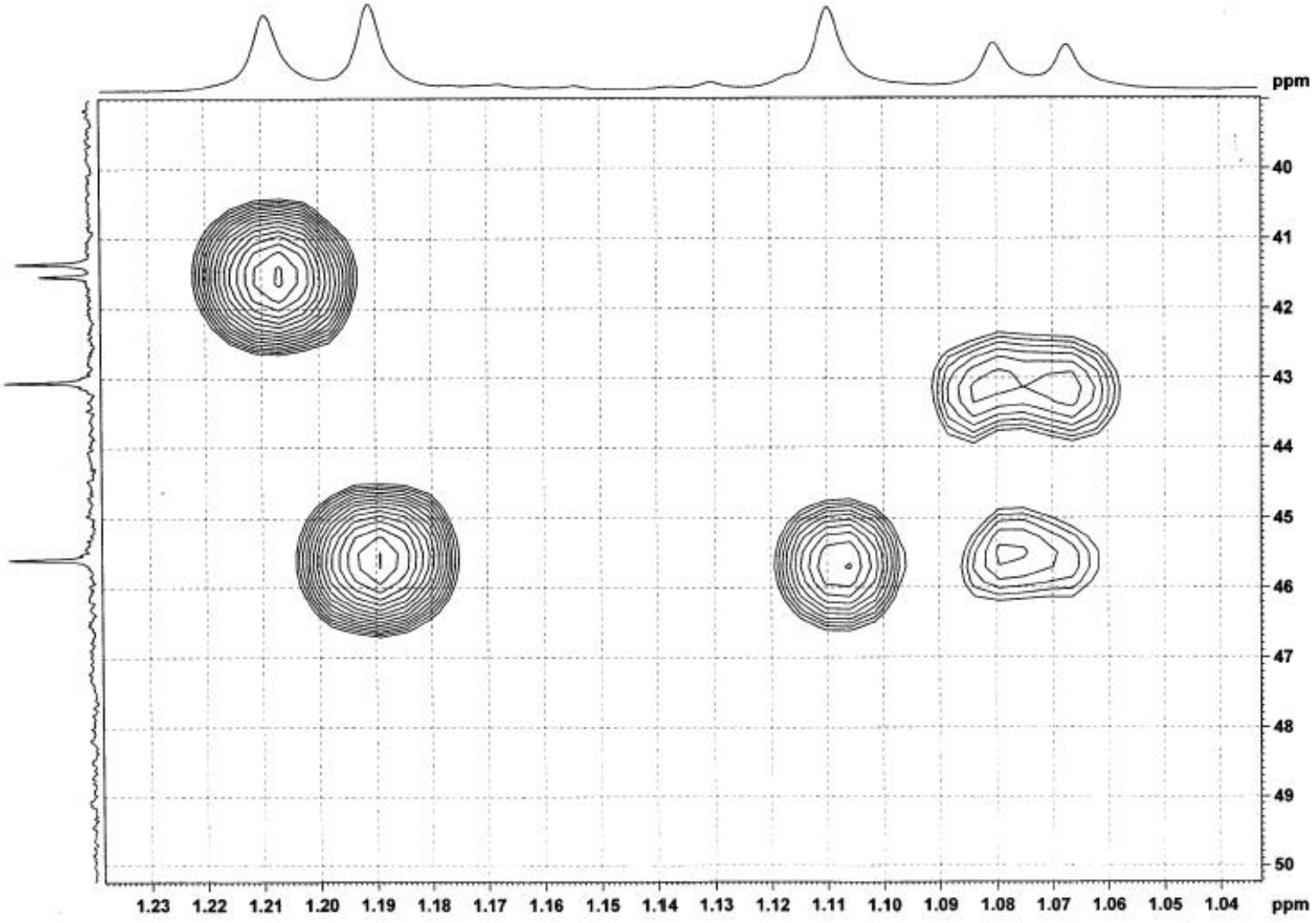
A Segment of HMBC Spectrum of xylogranatin R (**13**) in $CDCl_3$



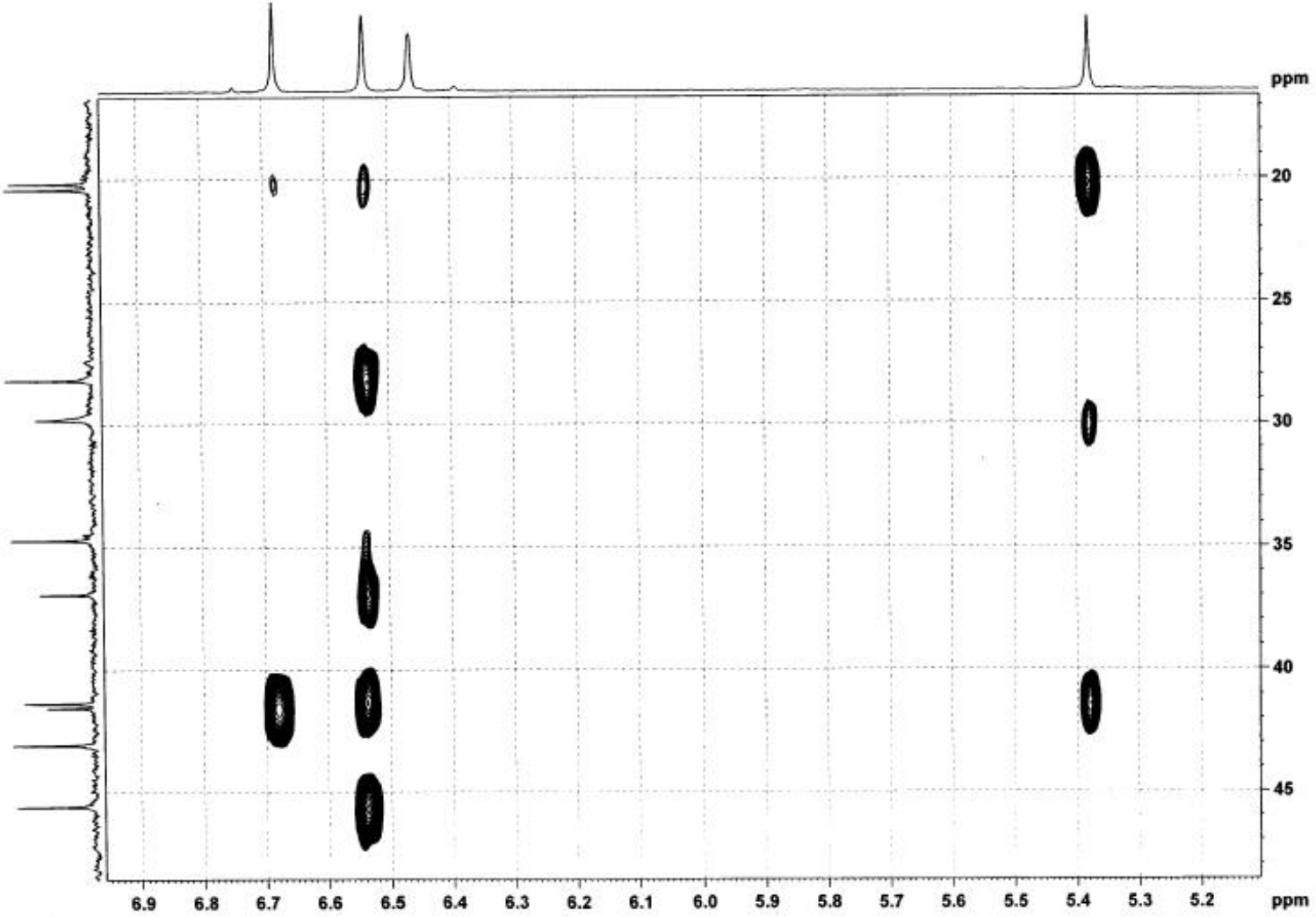
A Segment of HMBC Spectrum of xylogranatin R (**13**) in $CDCl_3$



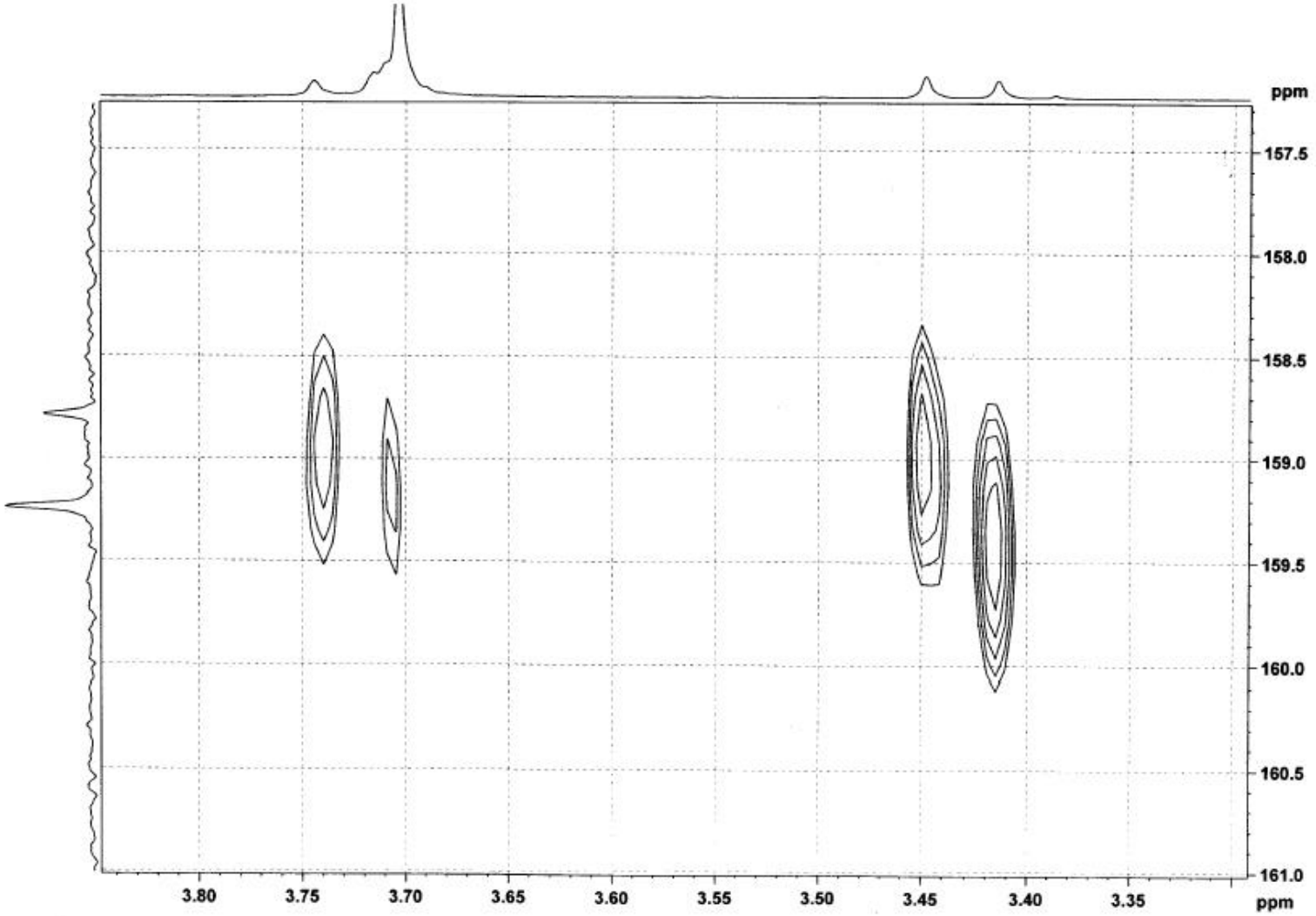
A Segment of HMBC Spectrum of xylogranatin R (**13**) in $CDCl_3$



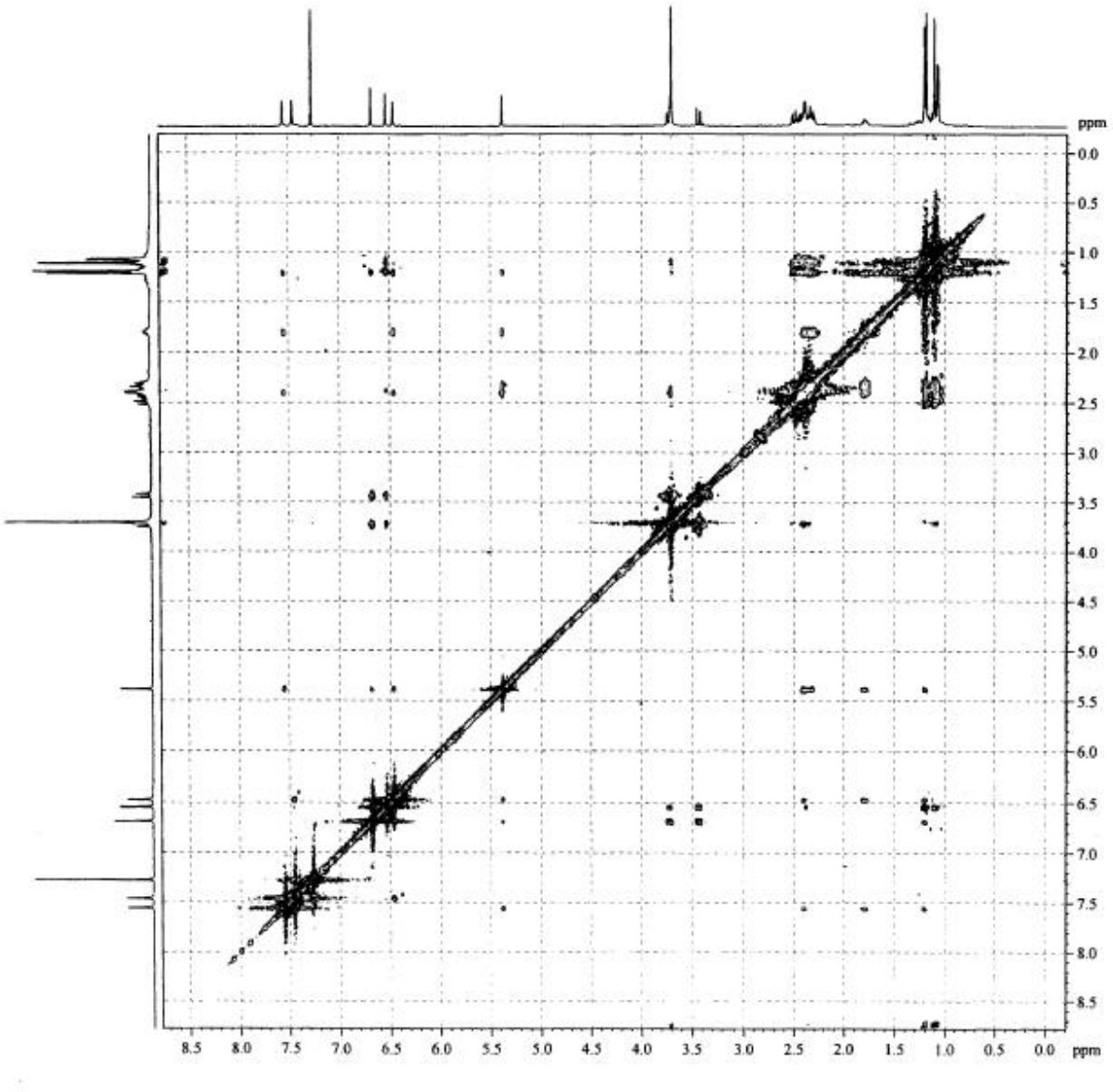
A Segment of HMBC Spectrum of xylogranatin R (**13**) in $CDCl_3$



A Segment of HMBC Spectrum of xylogranatin R (**13**) in $CDCl_3$



NOESY Spectrum of xylogranatin R (**13**) in $CDCl_3$



HR-TOFMS of xylogranatin C

Elemental Composition Report

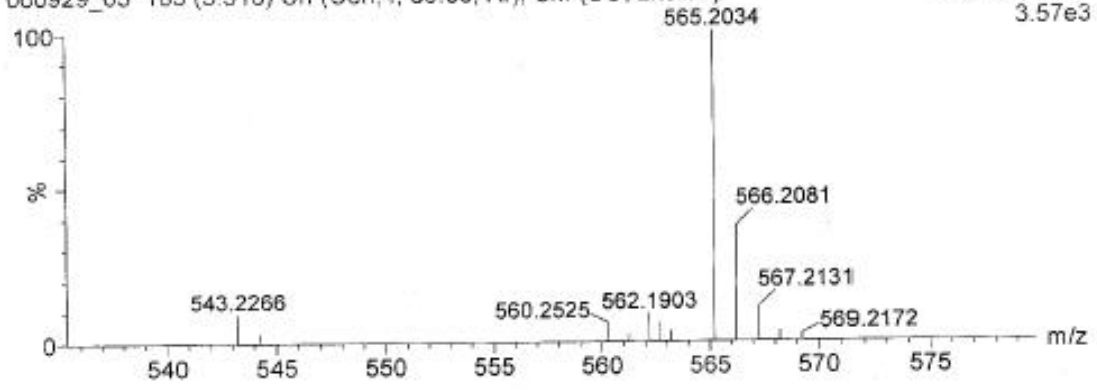
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
25 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

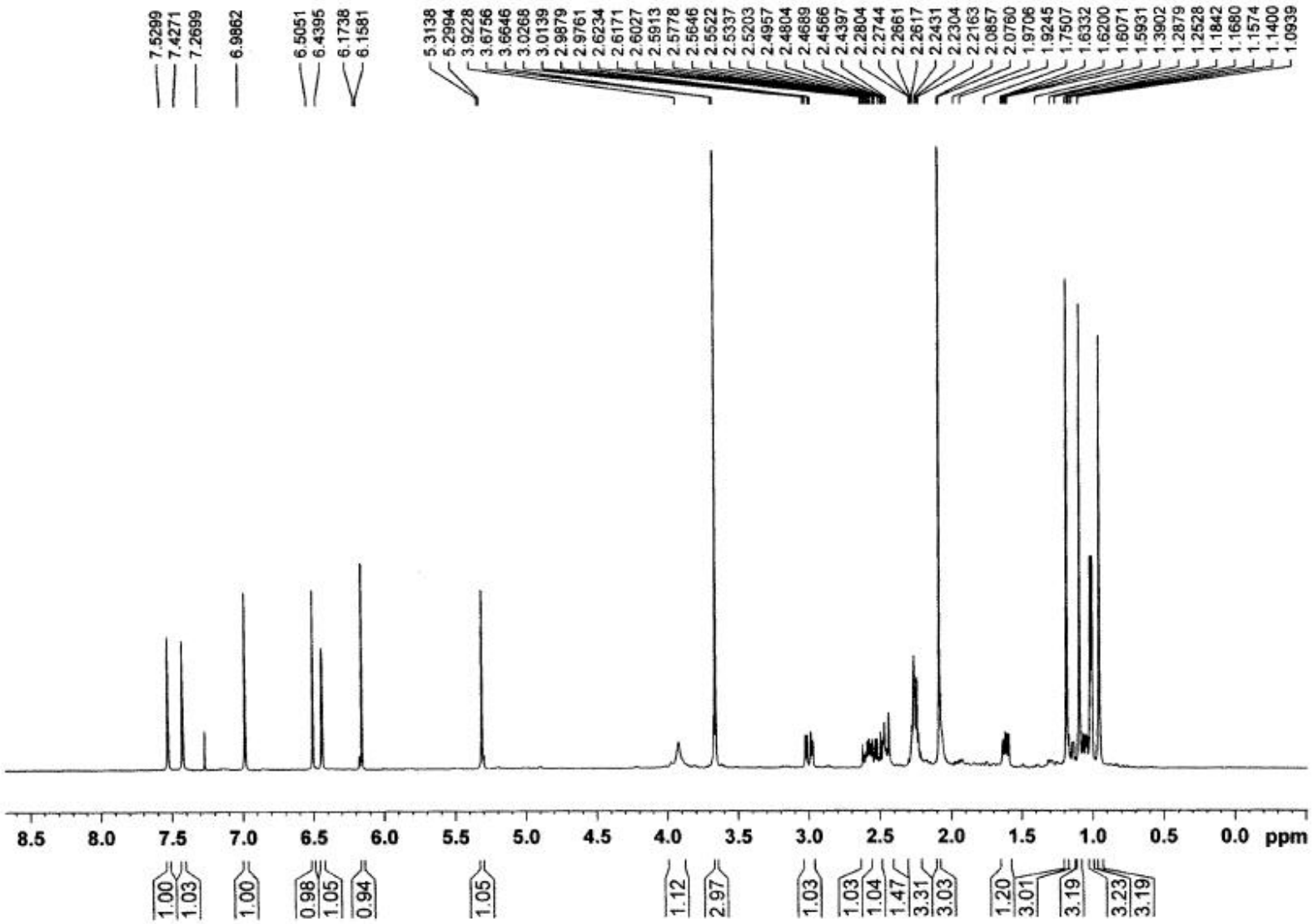
Minimum:				-1.5		
Maximum:		200.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
565.2034	565.2050	-1.6	-2.8	12.5	2	C29 H34 O10 23Na
	565.2074	-4.0	-7.0	15.5	1	C31 H33 O10

Wu09

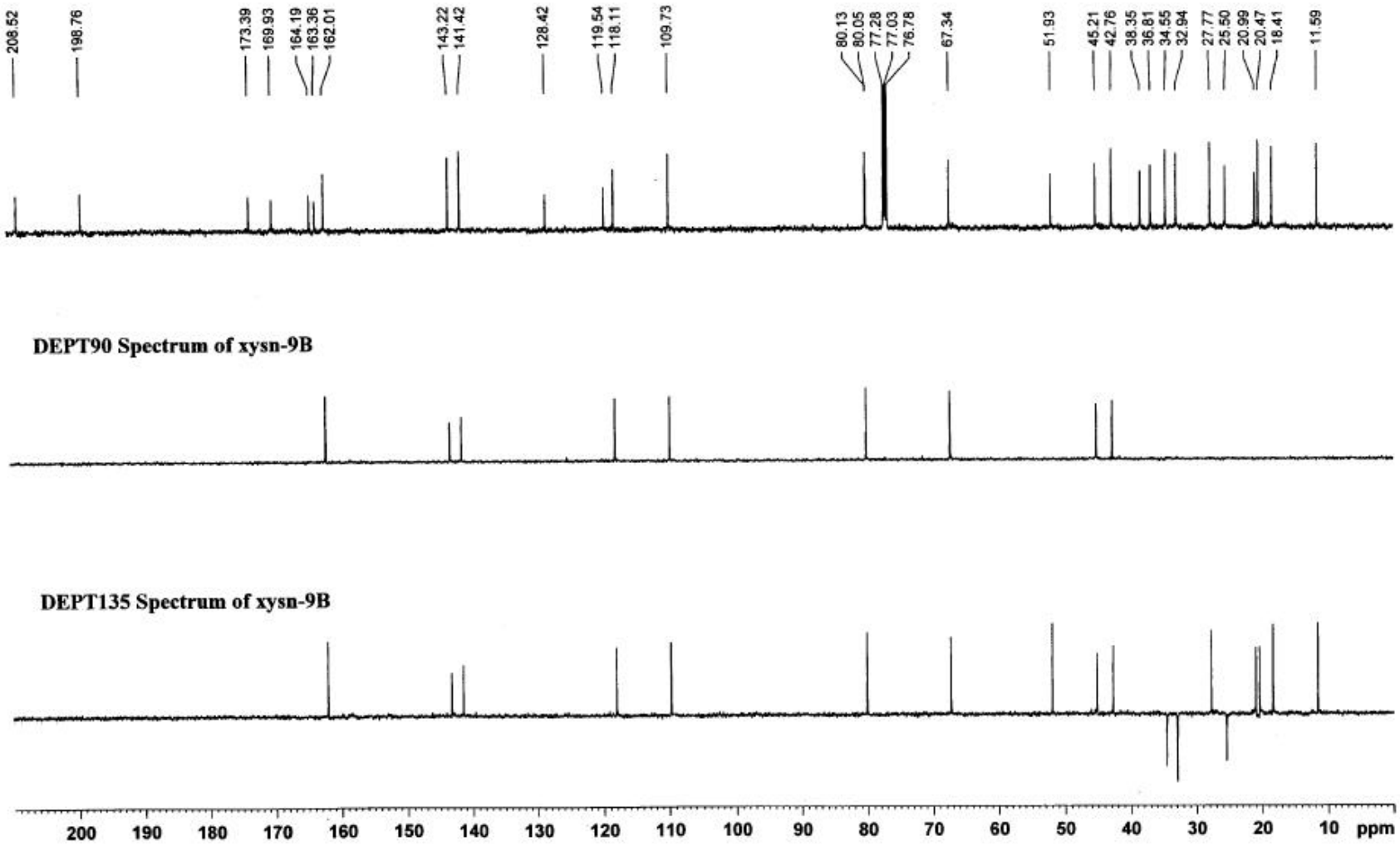
060929_03 185 (3.518) Cn (Cen,4, 80.00, Ar); Sm (SG, 2x3.00) TOF MS ES+ 3.57e3



^{1}H NMR (500 MHz) Spectrum of xylogranatin C in $CDCl_3$



^{13}C NMR (125 MHz) Spectrum and DEPT experiments of xylogranatin C in $CDCl_3$



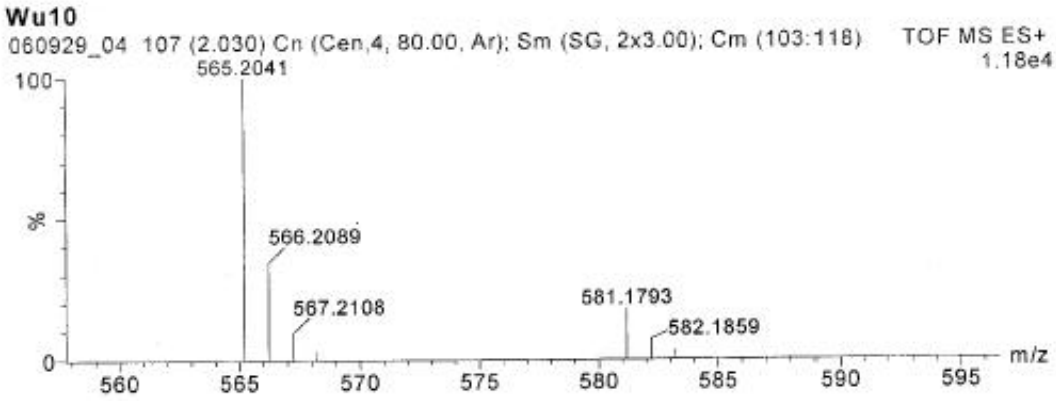
HR-TOFMS of xylogranatin D

Elemental Composition Report

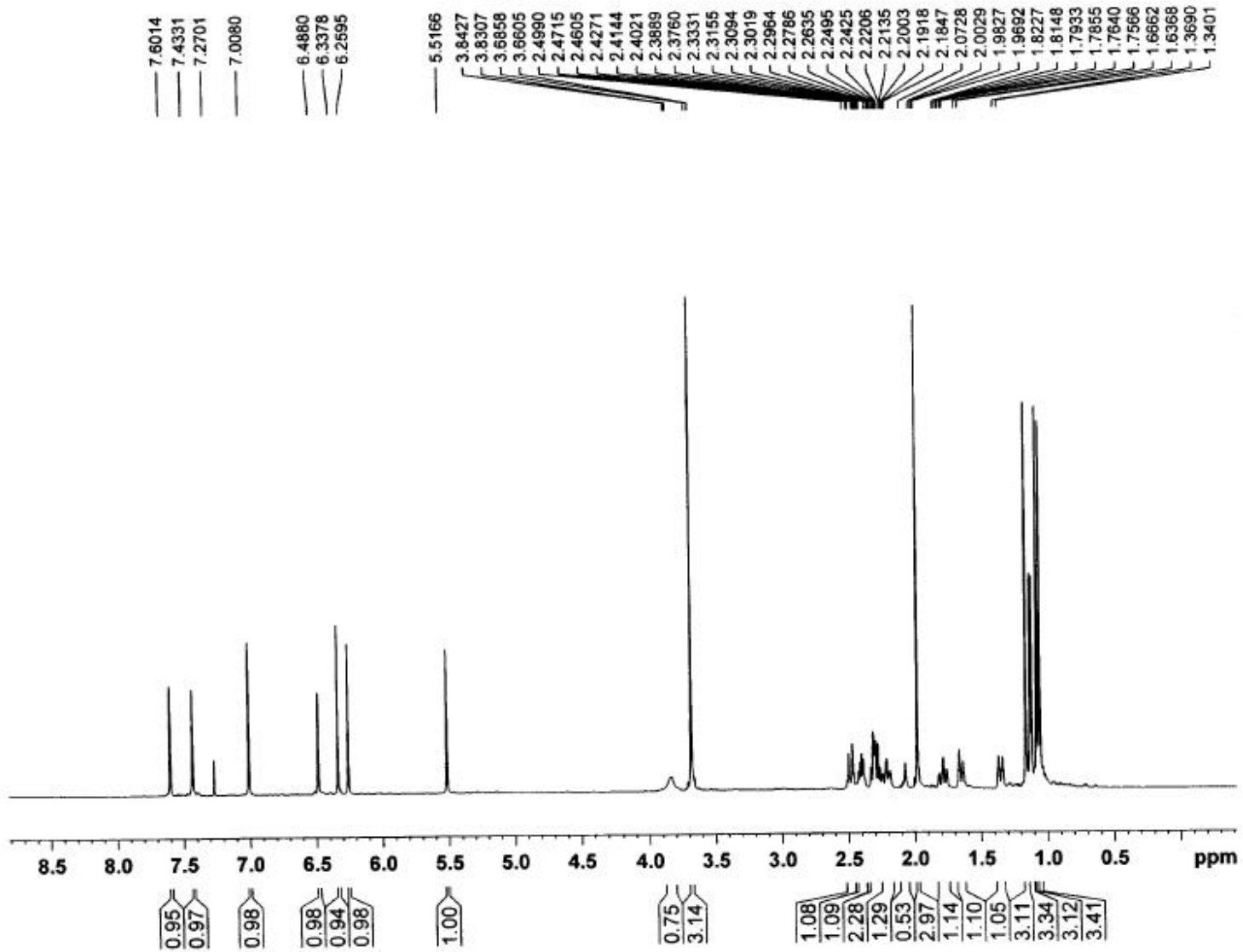
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
25 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

Minimum:				-1.5		
Maximum:		200.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
565.2041	565.2050	-0.9	-1.5	12.5	2	C29 H34 O10 23Na
	565.2074	-3.3	-5.8	15.5	1	C31 H33 O10



^{1}H NMR (500 MHz) Spectrum of xylogranatin D in $CDCl_3$



^{13}C NMR (125 MHz) Spectrum and DEPT experiments of xylogranatin D in $CDCl_3$