

Supporting Information

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A New Oleanane Type Saponin from the Aerial Parts of *Elaeocarpus hainanensis*

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S1: *General procedures*

Optical rotations were measured with a DIP-360 digital polarimeter (JASCO, Easton, USA). NMR spectra were recorded on a Bruker Avance 500 NMR spectrometer (BrukerSpin, Germany) at room temperature using standard pulse program, with tetramethylsilane as the internal standard and chemical shift values were expressed in δ (ppm). ESI-MS experiments employed an Agilent 1260 TripleQuad-6420 LC-MS/MS (Agilent Technologies, USA). HR-ESI-MS experiments employed a JEOL AccuTOFTM LC 1100 mass spectrometer (JEOL, Tokyo, Japan). Gas chromatography-GC (Shimadzu GC-2010 plus QP2020, Shimadzu Corp., Japan) using a Shimadzu SH-Rxi-5 Sil capillary column (0.25 mm ID \times 30 mm) [column temperature 210°C; detector temperature 300°C; injector temperature 270°C; He gas flow rate 30 mL/min (splitting ratio: 1/30)] was used for sugar determination. Column chromatography was performed on silica gel 60 (230–400 mesh, Merck, Darmstadt, Germany) and YMC ODS-A gel (50 μ m, YMC Co. Ltd., Kyoto, Japan). TLC was performed on Kieselgel 60 F₂₅₄ and TLC Silica gel 60 RP-18 F_{254S} (Merck, Damstadt, Germany) plates. Spots were visualized by spraying with 1% Ce(SO₄)₂-10% aqueous H₂SO₄ solution, followed by heating.

S2: Extraction and isolation

E. hainanensis sample (5.8 kg) was extracted with methanol (MeOH) at room temperature (3×20 L×24 h) and concentrated under vacuum at 55°C. The obtained residue (354.2 g) was suspended in water (1000 mL) and partitioned successively with *n*-hexane, dichloromethane (DCM), and *n*-BuOH (each 3 × 1000 mL) to obtain residues of *n*-hexane (23.8 g), DCM (80.4 g), and *n*-BuOH (28.70 g). Next, the BuOH portion (25 g) was subjected to a silica gel column (Φ60 mm × 80 mm) with stepwise gradient of CH₂Cl₂-MeOH (5:1→1:1, v/v, 600 mL/fraction) to obtain 4 fractions (B1~B4). Fr. B3 (3.7 g) was then loaded onto a silica gel column (Φ 45 mm × 350 mm) with an eluent of CHCl₃-MeOH-H₂O (3:1:0.1, v/v/v, 1500 mL) to yield four sub-fractions (fr. B3.1~B3.4). Fr. B3.2 (750 mg) was further purified on a reversed-phase C₁₈ column (Φ30 mm × 400 mm) with MeOH-H₂O (2:3, v/v, 1000 mL) to obtain compound **1** (15.5 mg).

S3: *Acid hydrolysis and sugar determination*

A solution of the new compound (2.0 mg) in HCl 1.0 M (3.0 mL) was heated under reflux for 2 h. Then, the reaction mixture was concentrated *in vacuum* to dryness. The residue was extracted with CHCl₃ and H₂O (5 ml each, 3 times). Next, the sugar residue obtained by concentration of the water layer was dissolved in dry pyridine (0.1 mL). Then L-cysteine methyl ester hydrochloride in pyridine (0.06 M, 0.1 mL) was added to the solution. After heating the reaction mixture at 60°C for 2 h, 0.1 mL of trimethylsilylimidazole was added. Heating at 60°C was continued for a further 2 h, and the mixture was evaporated *in vacuum* to give a dried product, which was partitioned between *n*-hexane and H₂O. The *n*-hexane layer was analyzed using the GC procedure (General Procedures). The peaks of the hydrolysates of the respective glycosides were detected at t_R 4.50 min (L-arabinose). The retention time for the authentic sample L-arabinose (Sigma) after being treated similarly was 4.50 min (L-arabinose). Co-injection of the hydrolysate of the compound with standard L-arabinose gave single peak.

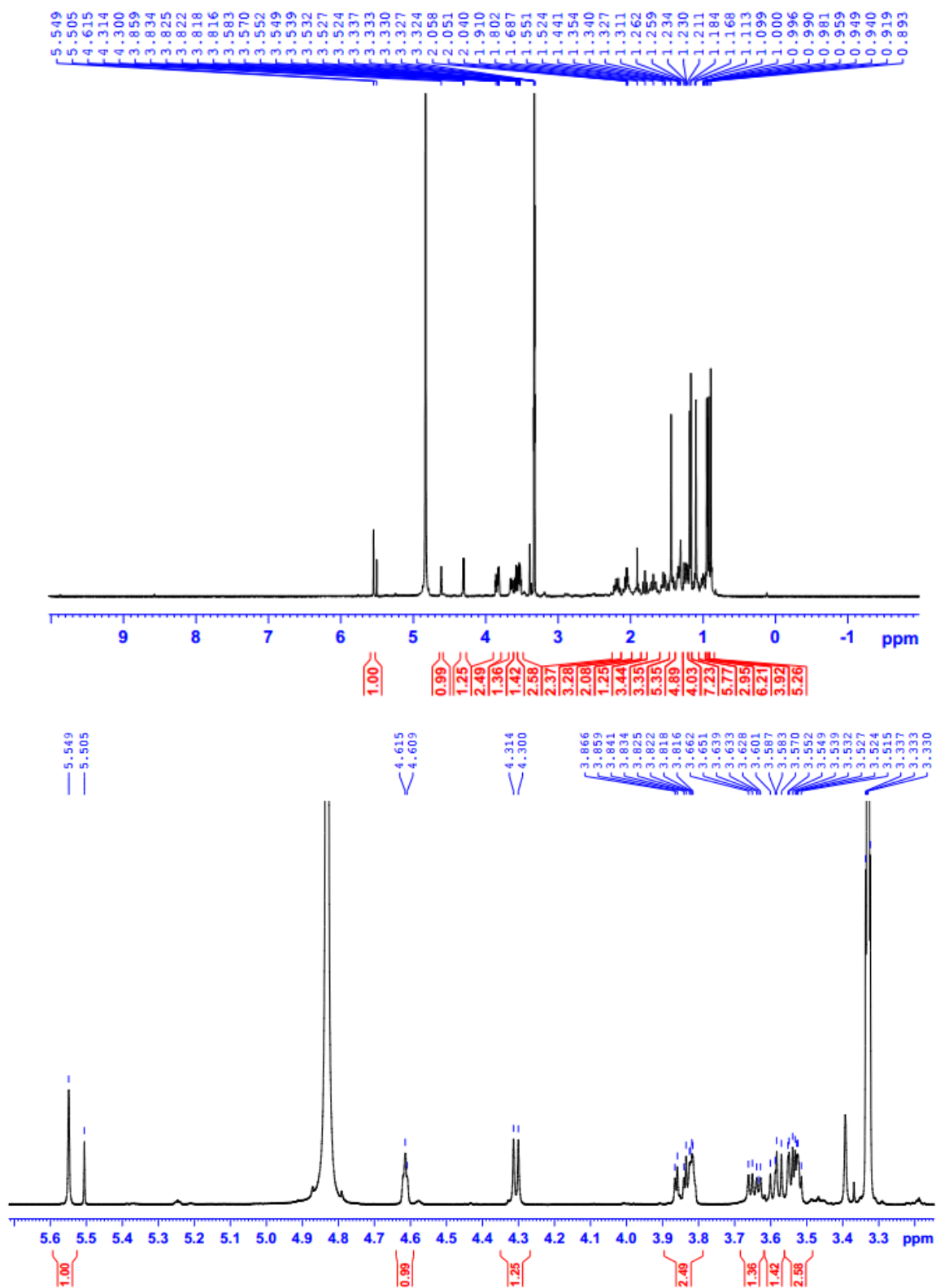


Figure S1: The ^1H NMR (500 MHz, CD_3OD) spectrum of **1**

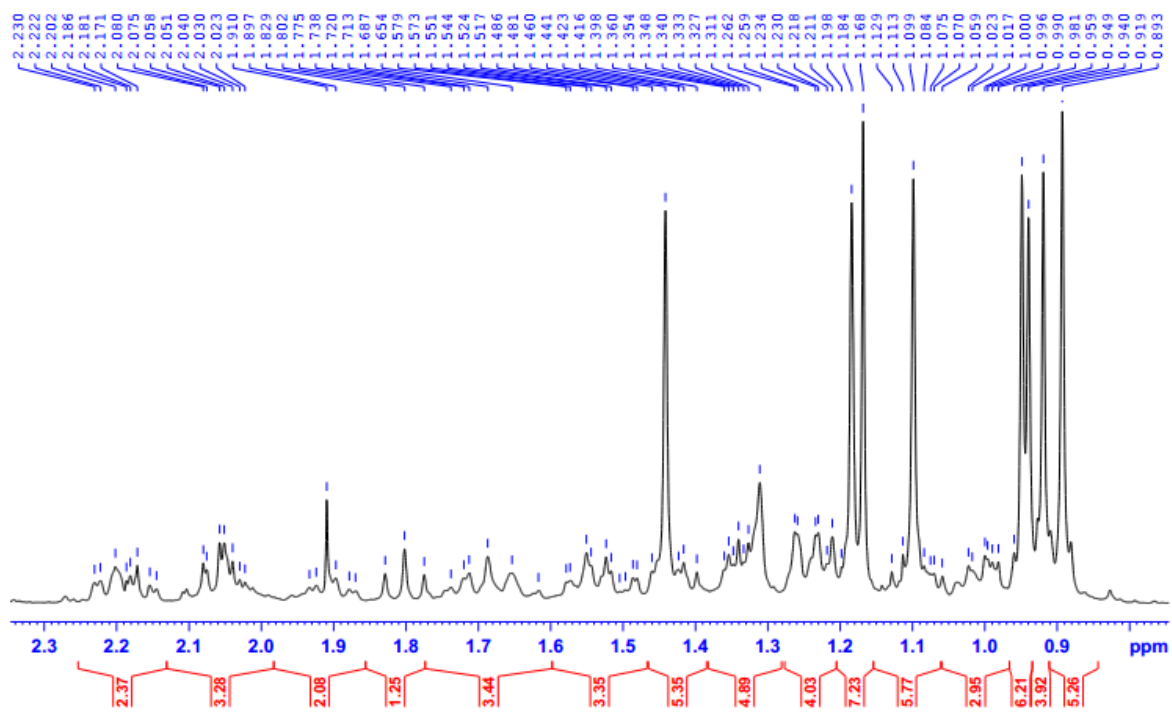


Figure S1: The ^1H NMR (500 MHz, CD_3OD) spectrum of **1** (expanded)

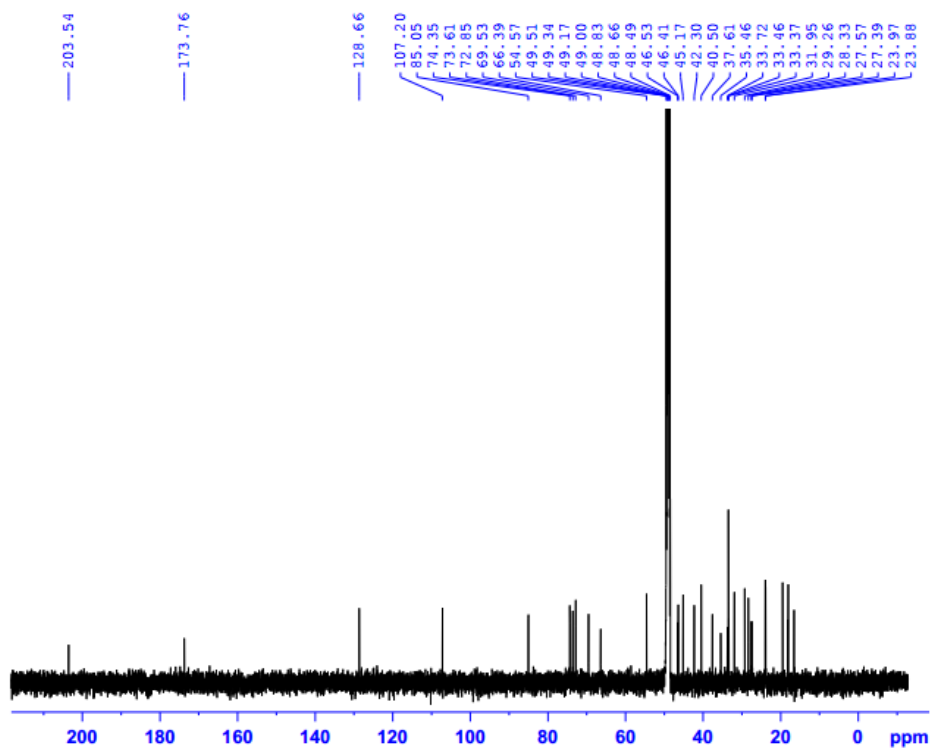


Figure S2: The ^{13}C NMR (125 MHz, CD_3OD) spectrum of **1**

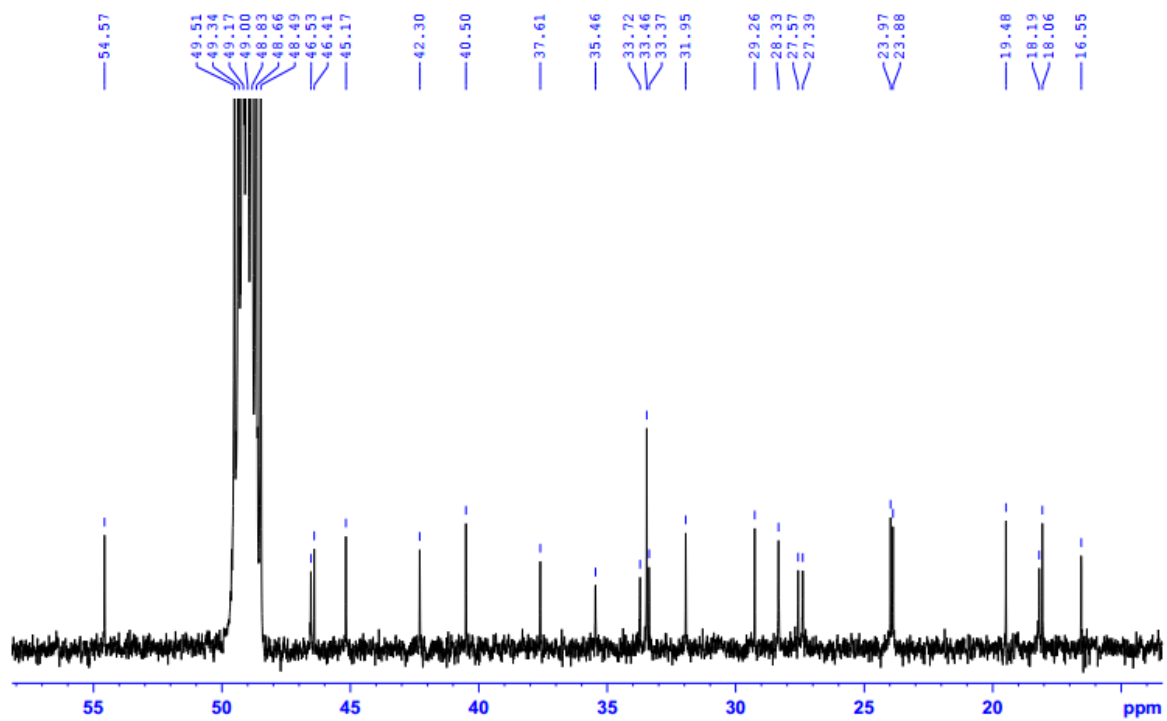
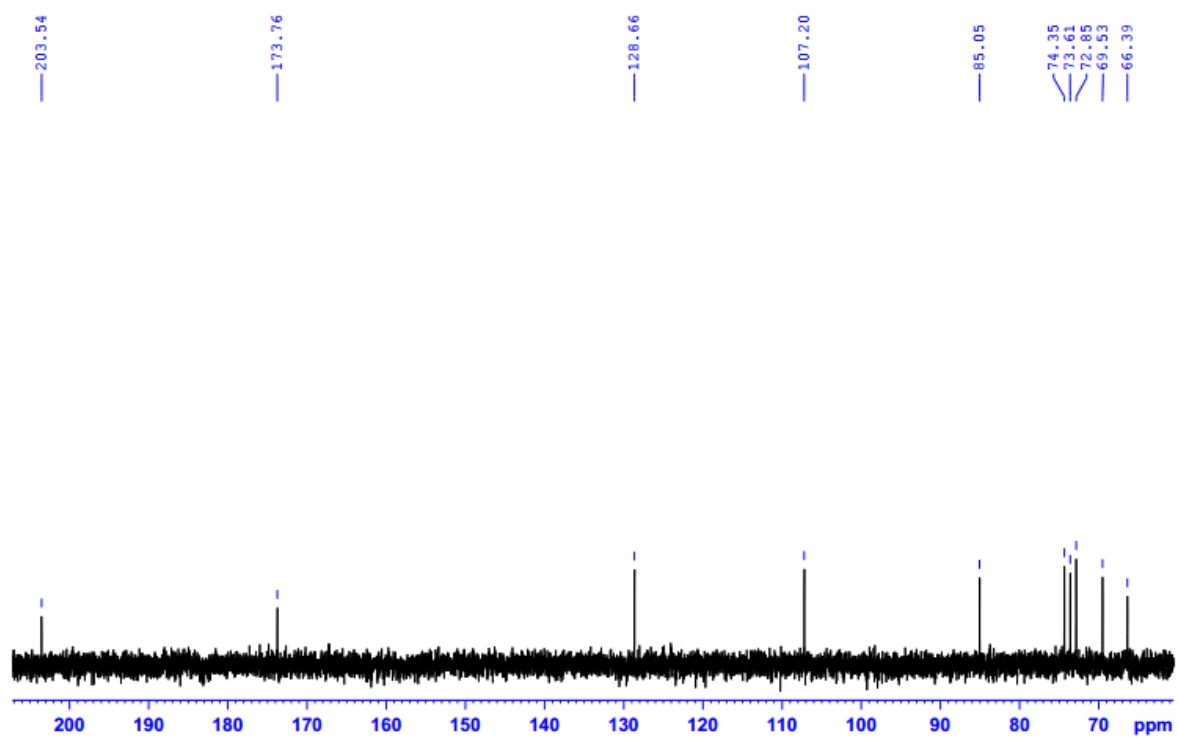
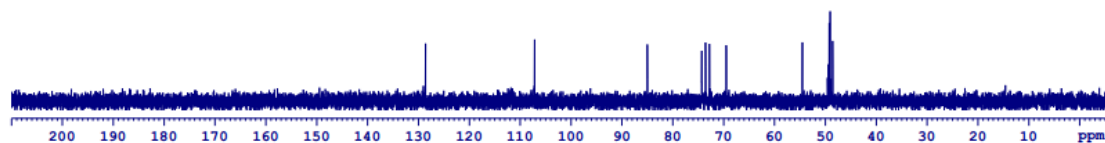


Figure S2: The ^{13}C NMR (125 MHz, CD_3OD) spectrum of **1** (*expanded*)

DEPT90

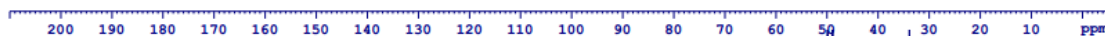


DEPT135

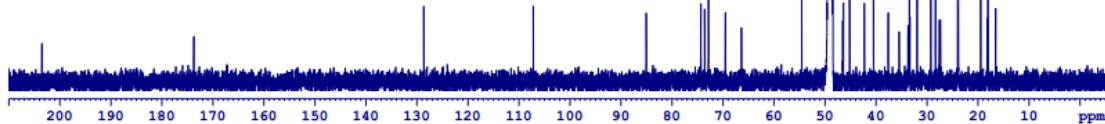


CH&CH3

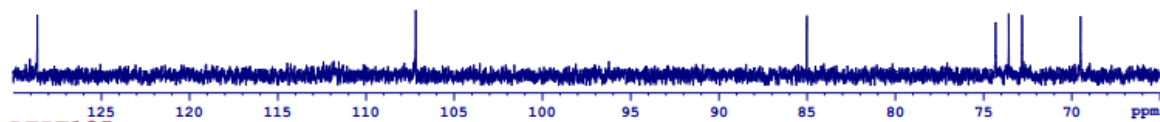
CH2



C13CPD



DEPT90



DEPT135



CH&CH3

CH2



C13CPD

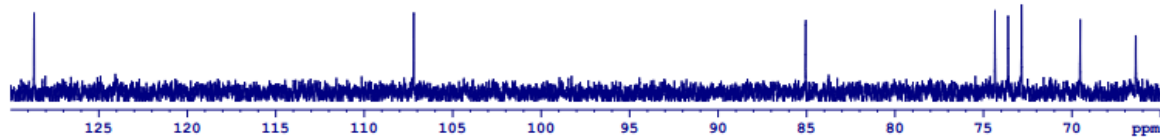


Figure S3: The DEPT spectrum of 1

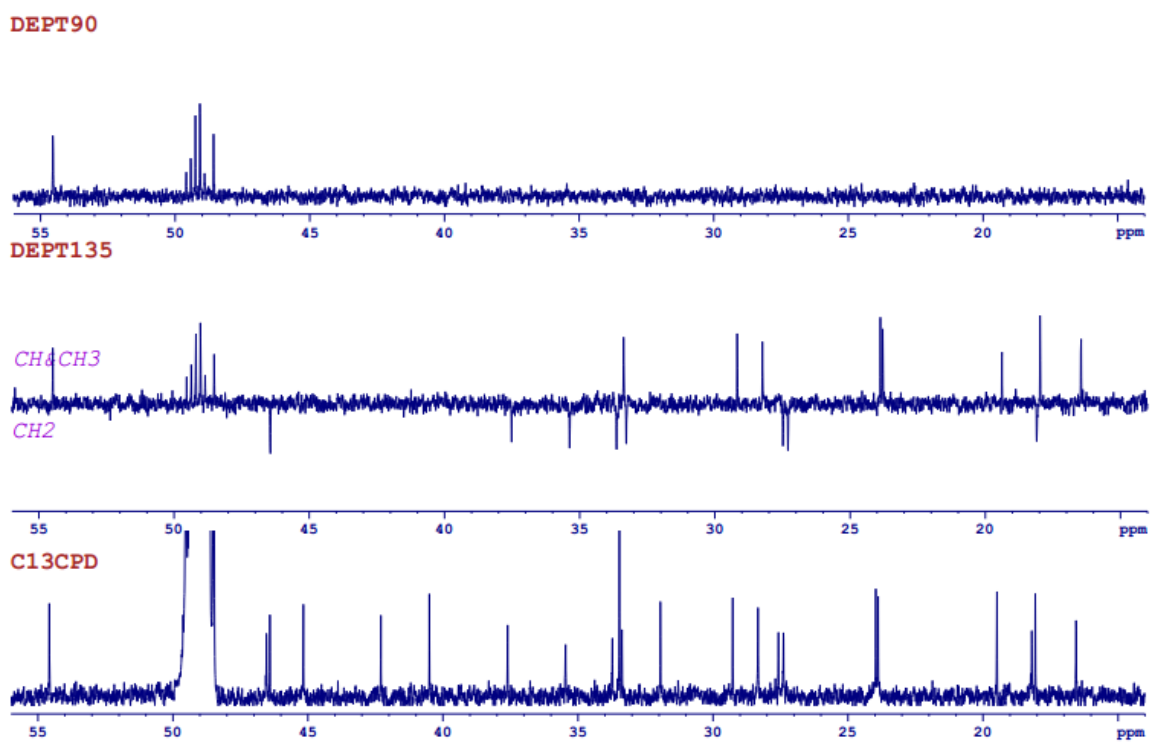


Figure S3: The DEPT spectrum of **1** (*expanded*)

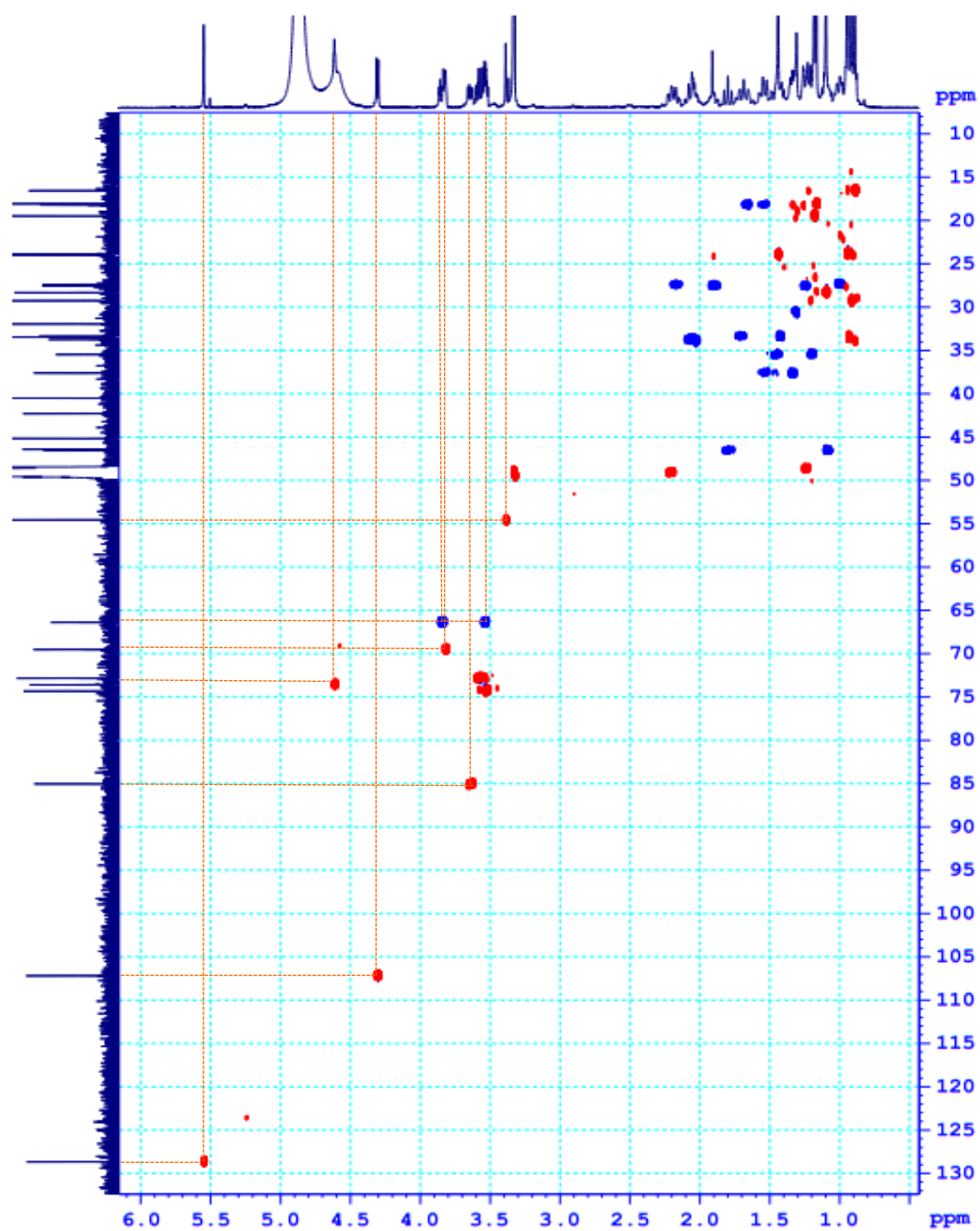


Figure S4: The HSQC spectrum of **1**

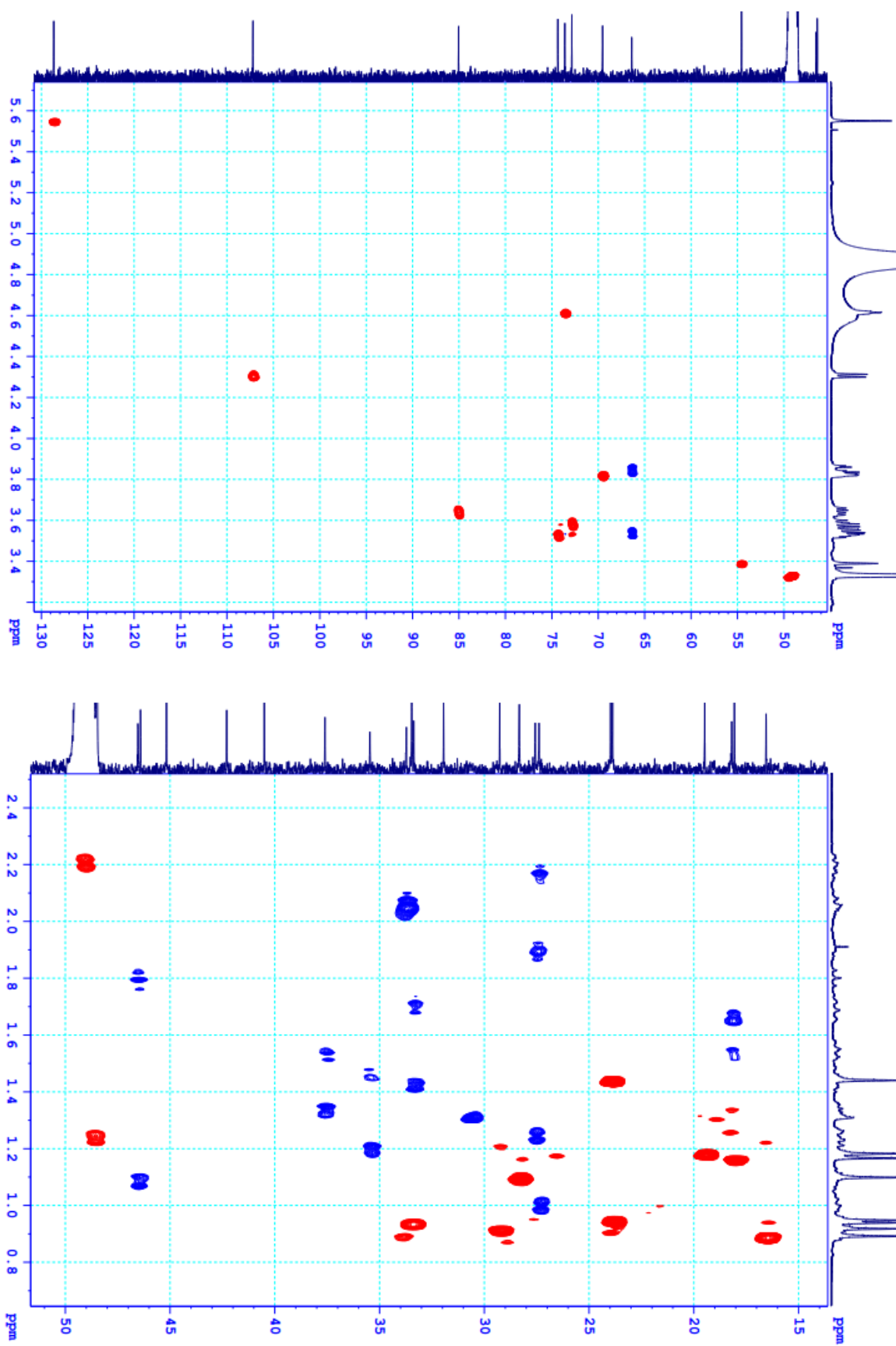


Figure S4: The HSQC spectrum of **1** (*expanded*)

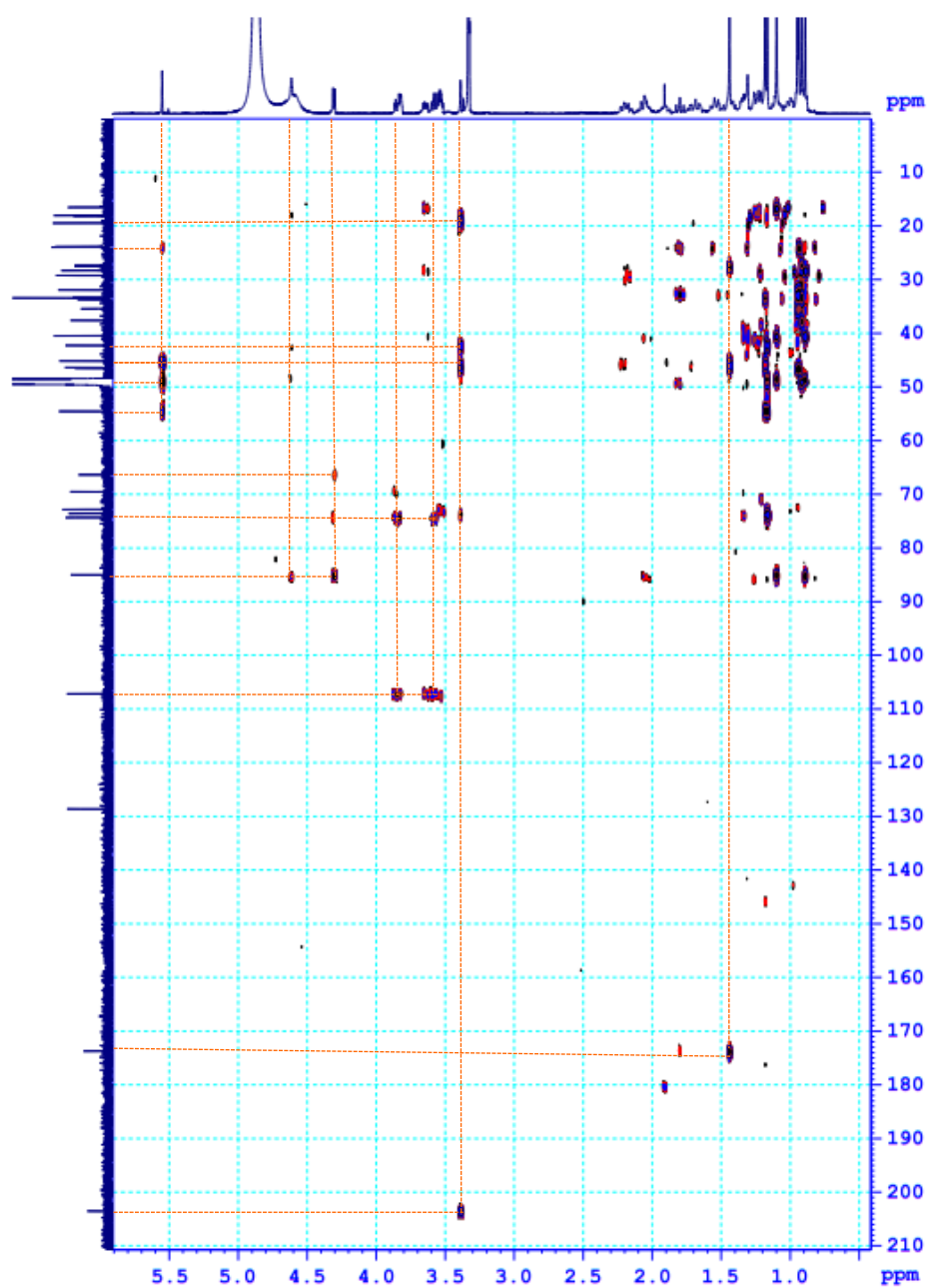


Figure S5: The HMBC spectrum of **1**

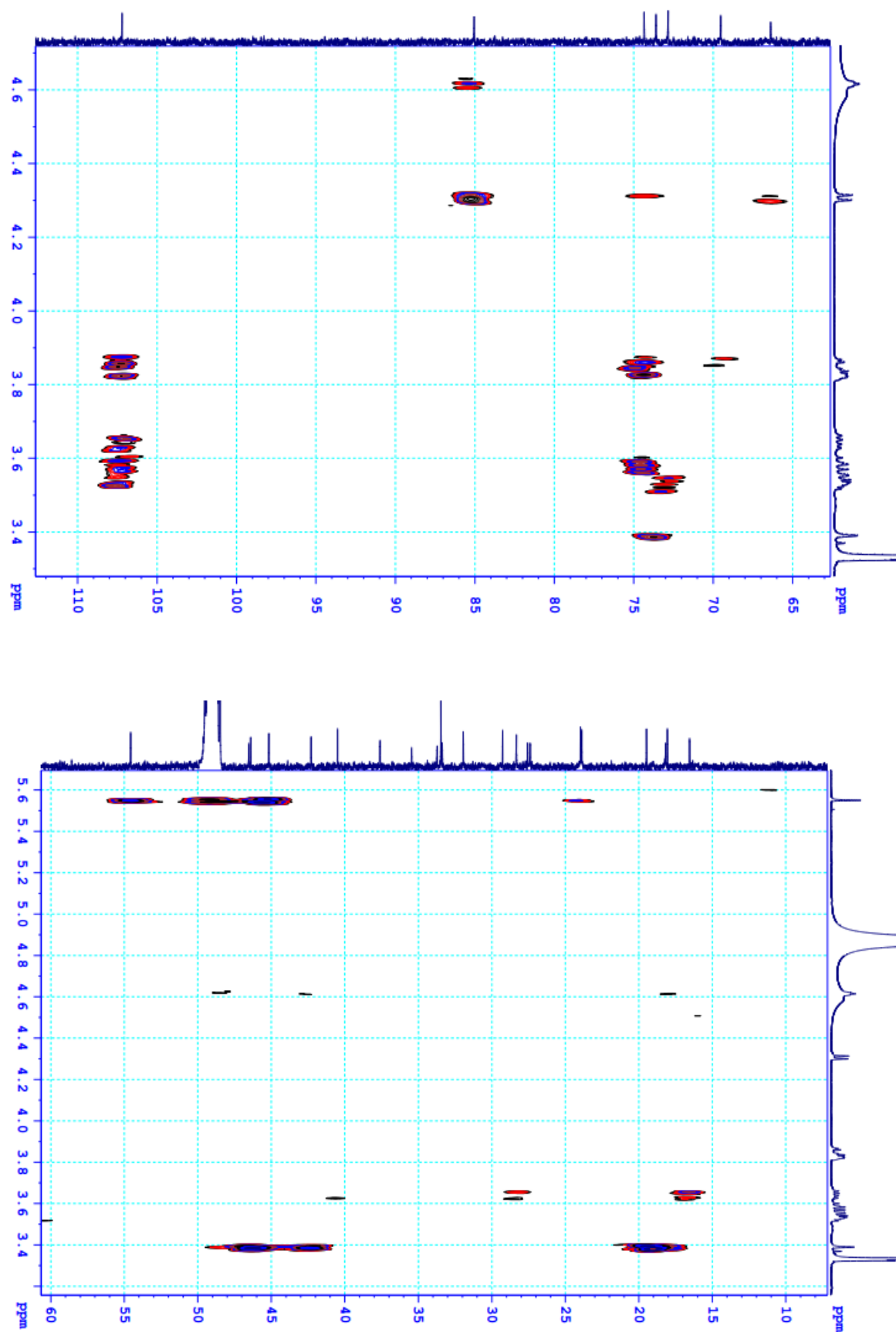


Figure S5: The HMBC spectrum of **1** (*expanded*)

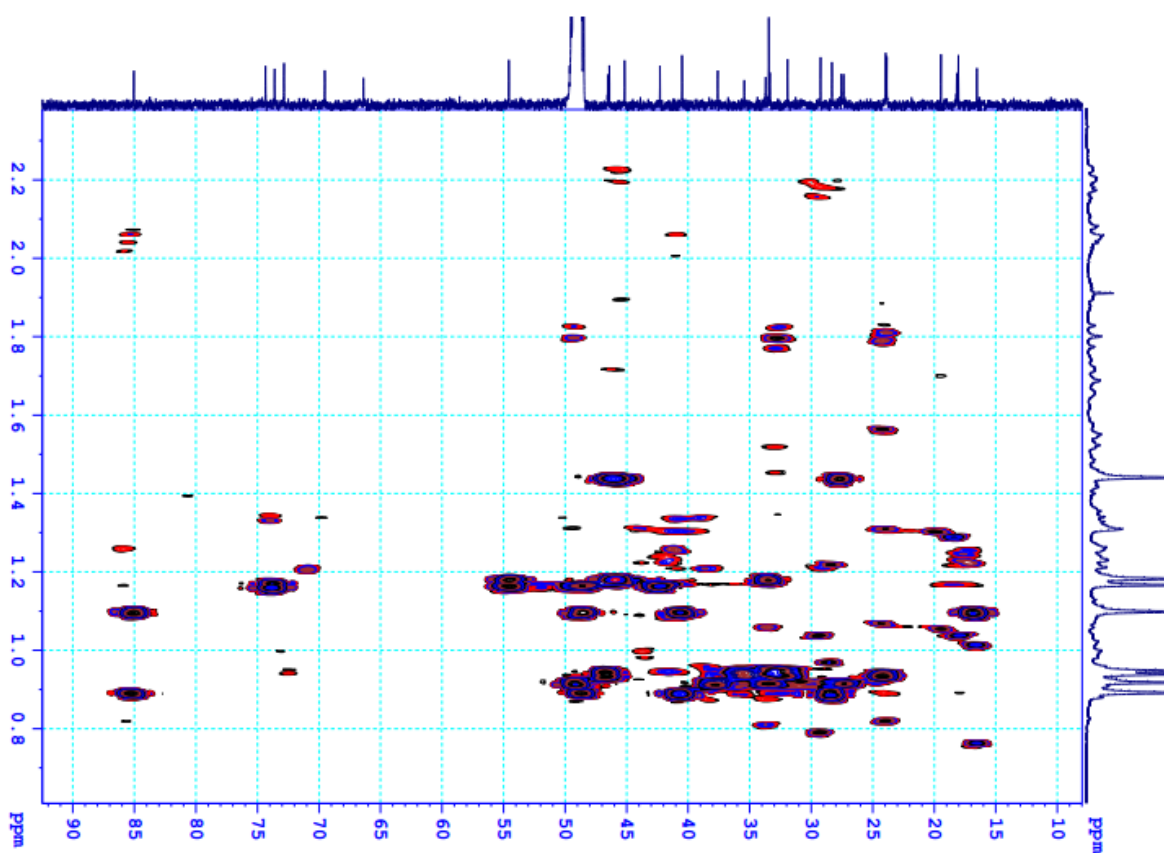
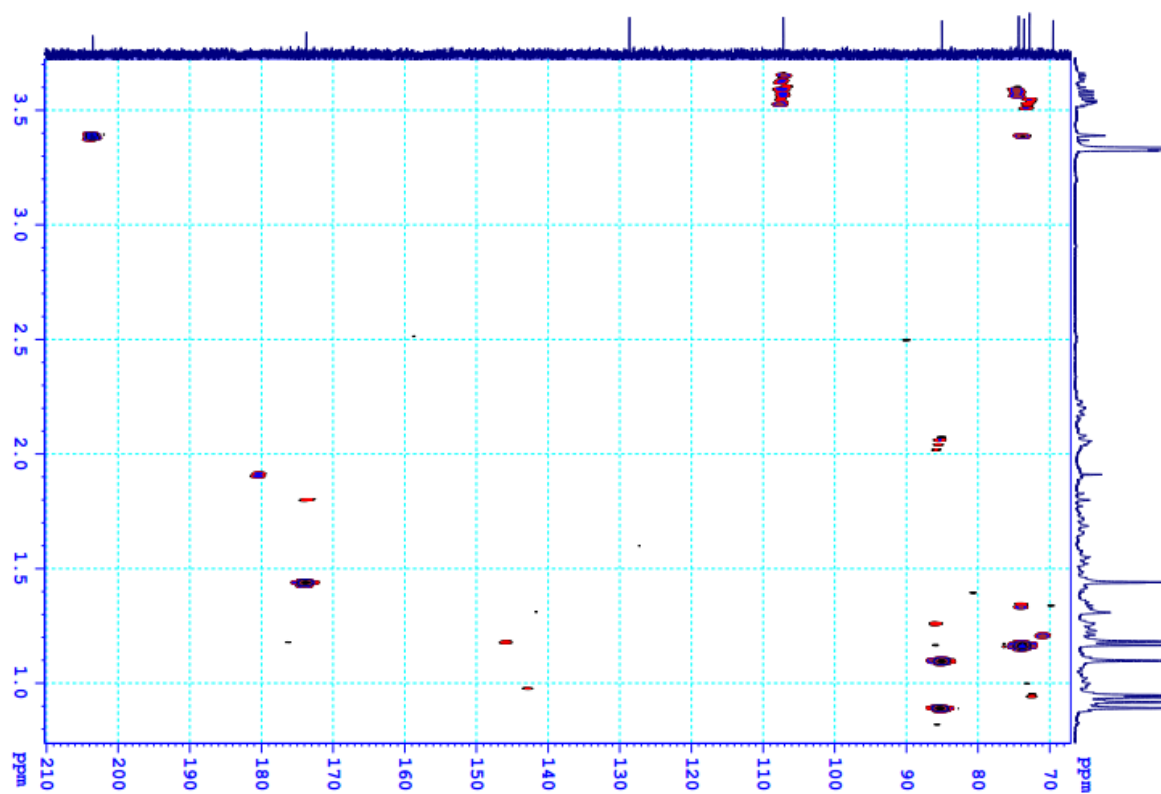


Figure S5: The HMBC spectrum of **1** (*expanded*)

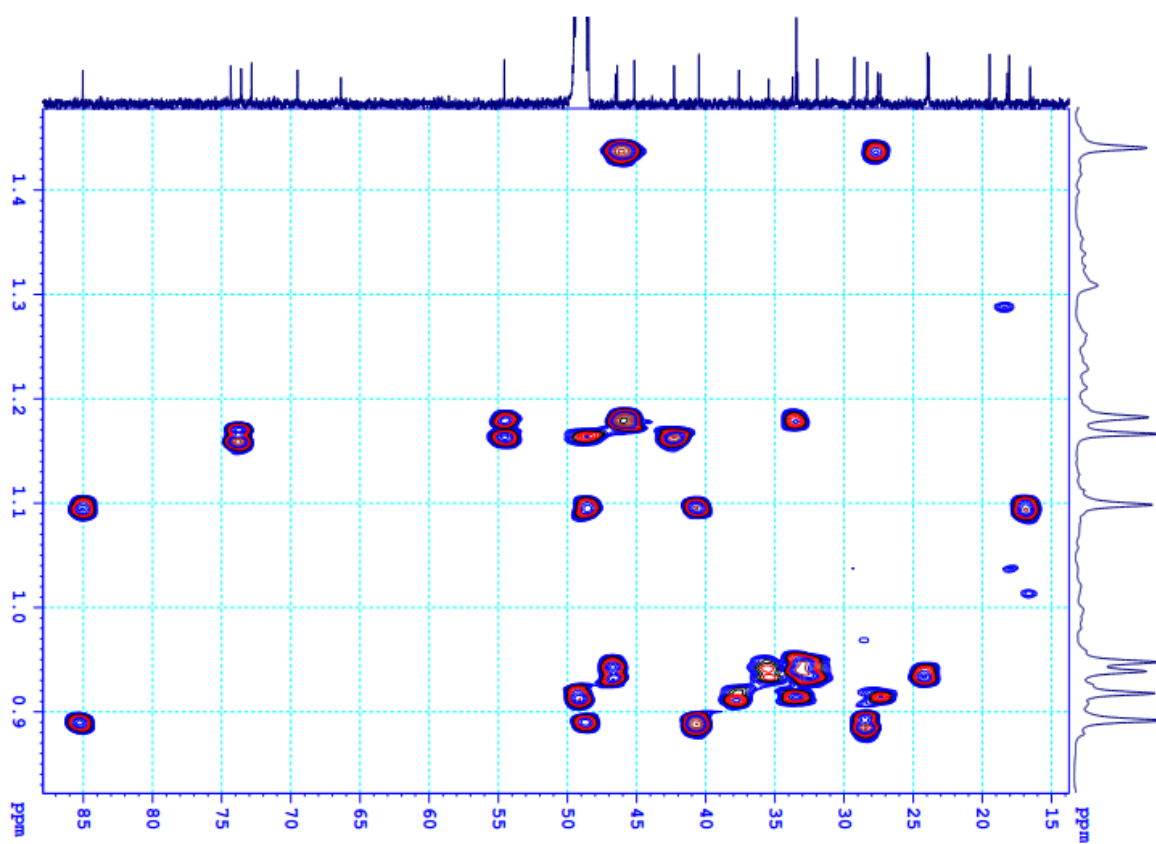


Figure S5: The HMBC spectrum of **1** (*expanded*)

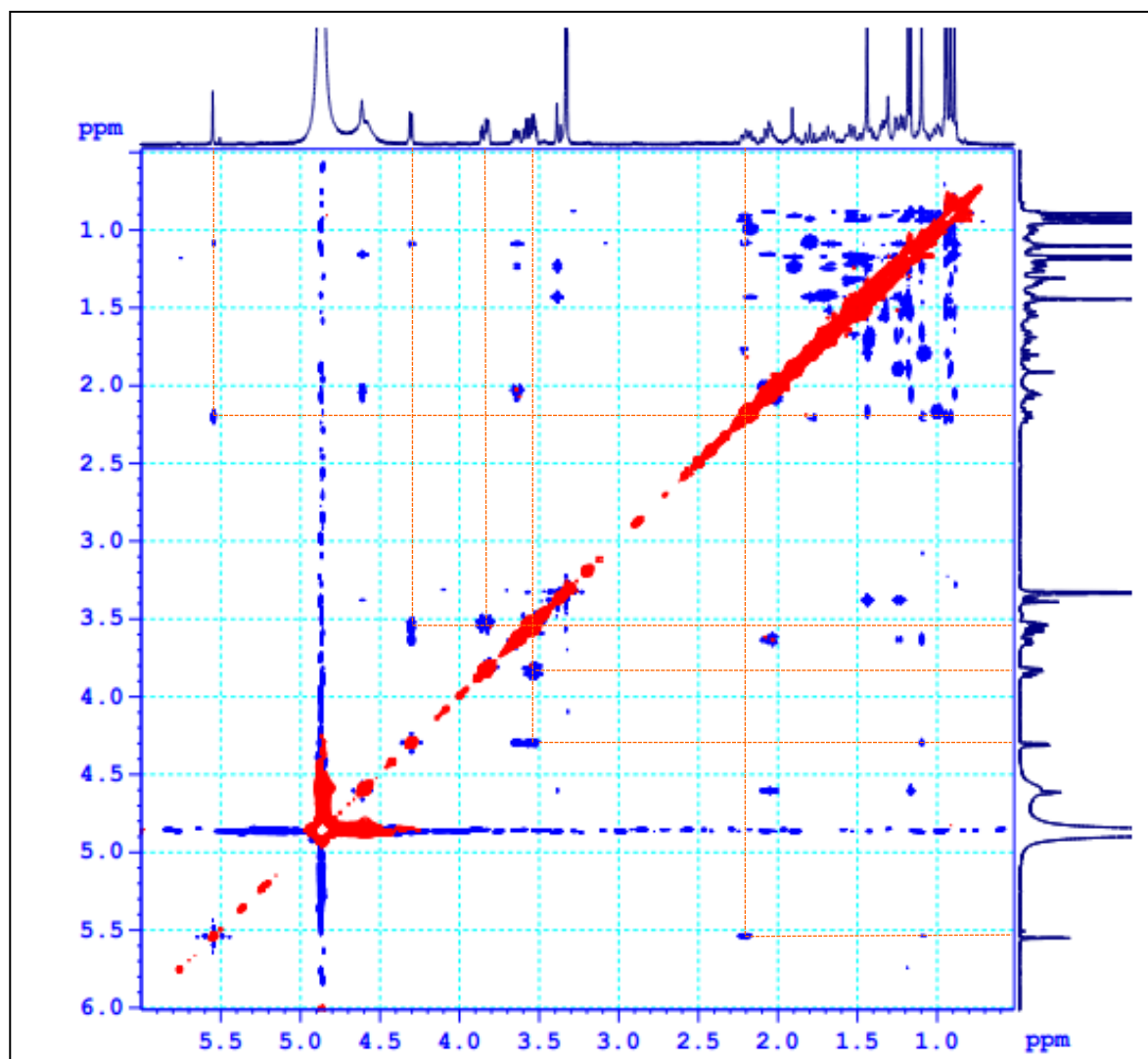


Figure S6: The NOESY spectrum of **1**

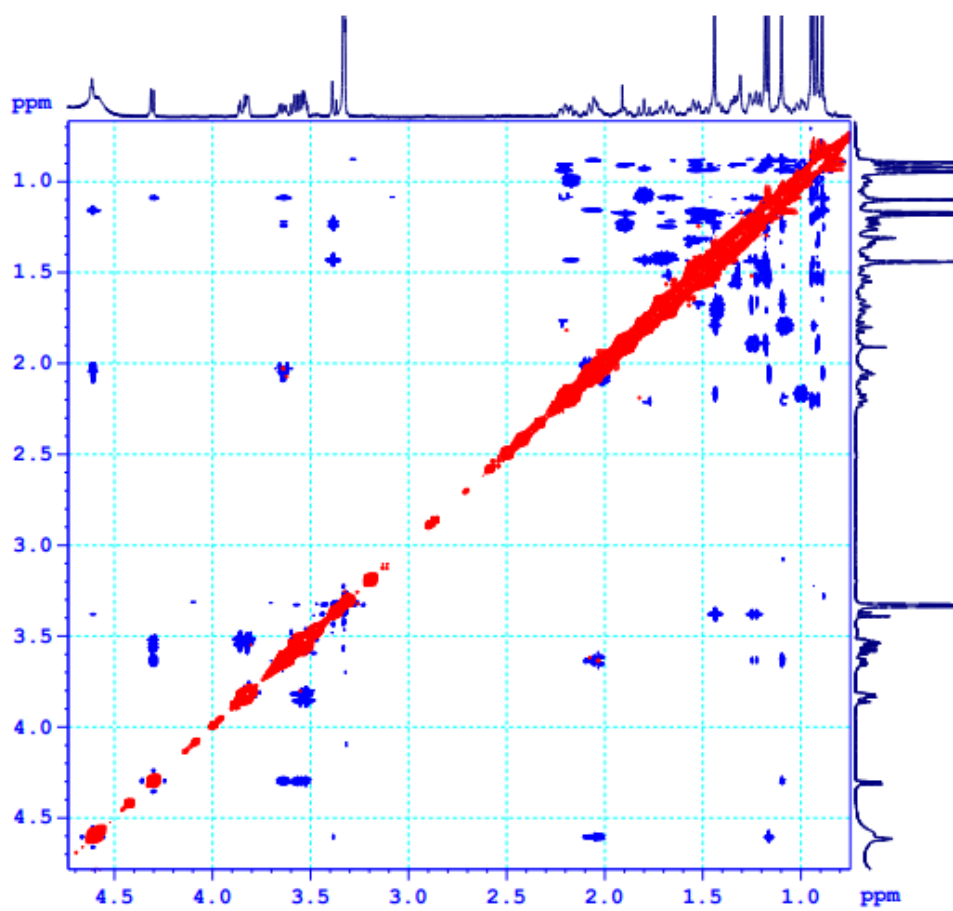


Figure S6: The NOESY spectrum of **1** (*expanded*)

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

209 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)

Elements Used:

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	C	H	O
589.4132	589.4104	2.8	2.3	4.4	C35 H57 O7	2.9	35	57	7

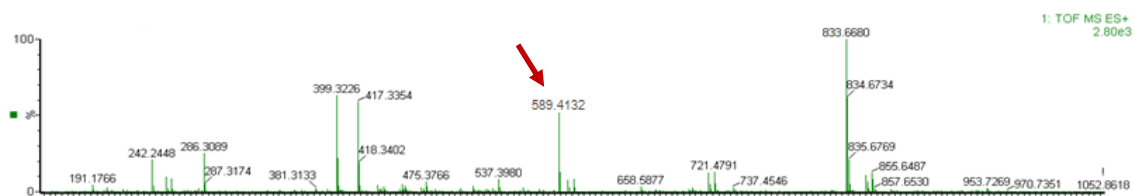


Figure S7: The HR-MS spectrum of **1**

The image displays a screenshot of the SciFinder software interface. The main window is titled "SciFinder" and shows a search page for "Substance (20)". The search type is set to "Exact Structure". A chemical structure is shown in the center, and a "Check for Similarity" button is visible. The right side of the image shows a separate window with a chemical structure.

Figure S8: SciFinder check for the new compound

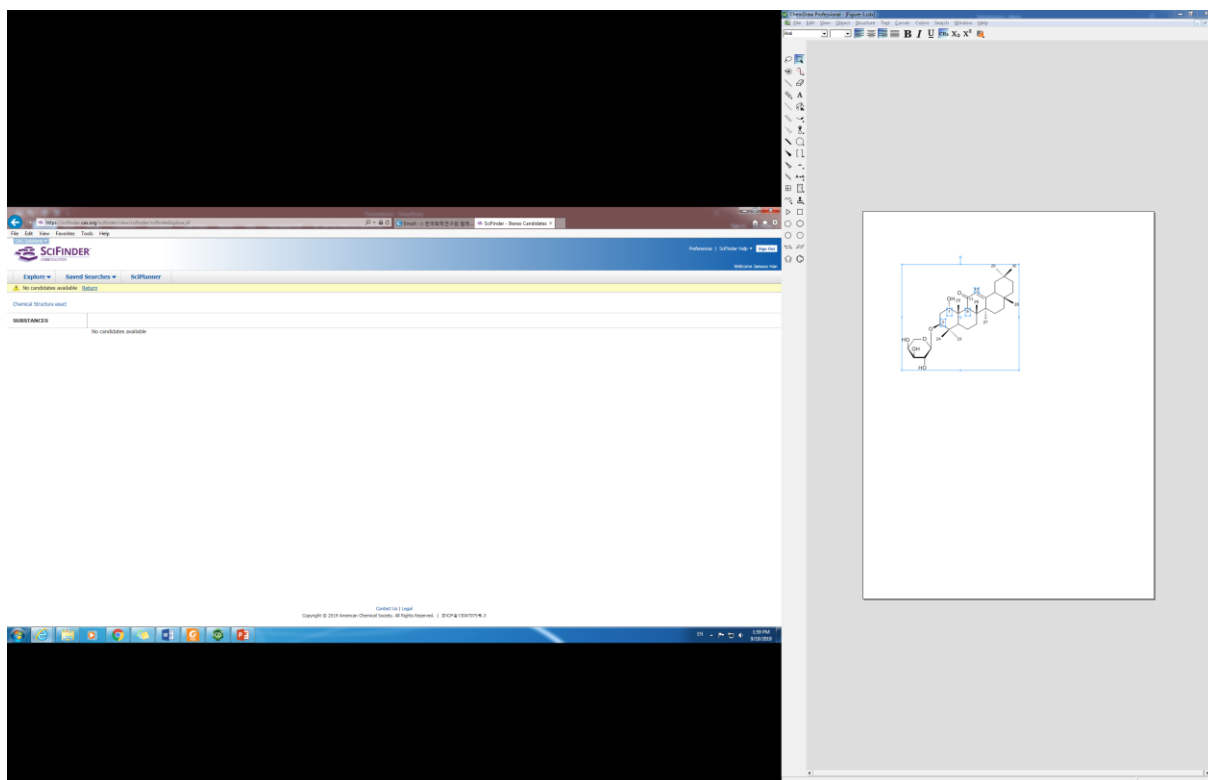
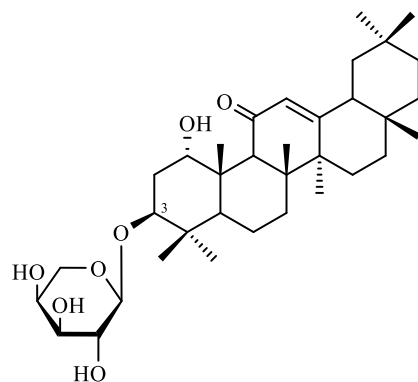
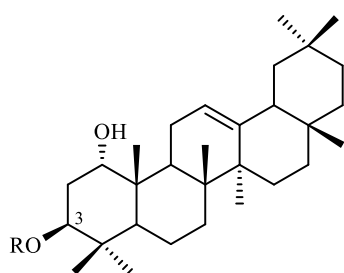


Figure S8: SciFinder check for the new compound (*continued*)

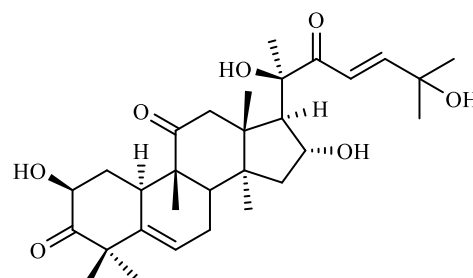


1a-hydroxy-olean-11-oxo-12-en-3-O-b-L-arabinopyranoside (**1**, the new compound)

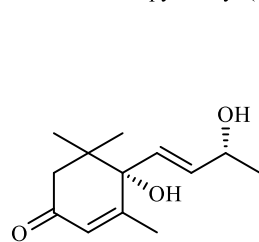


R = -*b*-D-xylopyranosyl (1a-hydroxy-olean-12-en-3-O-b-D-xylopyranoside)

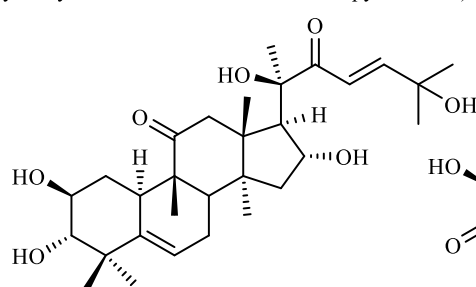
R = -*b*-L-arabinopyranosyl (1a-hydroxy-olean-12-en-3-O-b-L-arabinopyranoside)



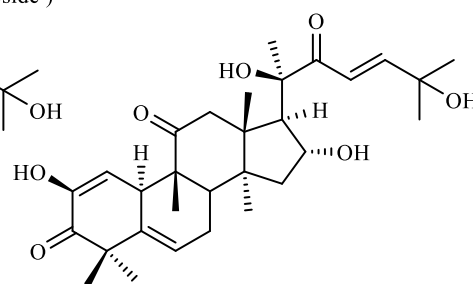
Cucurbitacin D



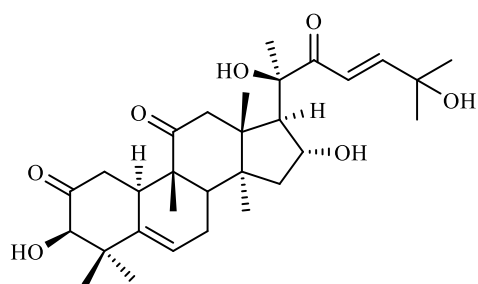
Blumenol



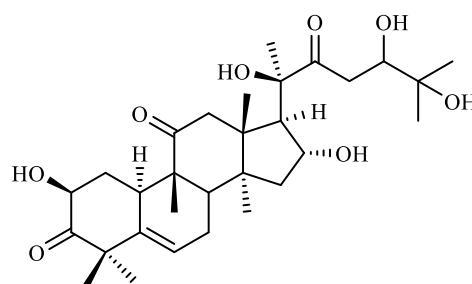
Cucurbitacin F



Cucurbitacin I



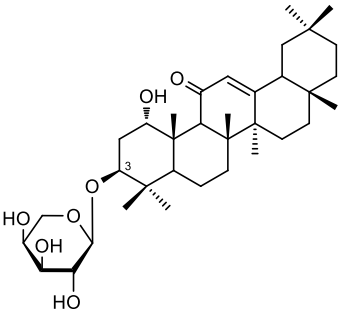
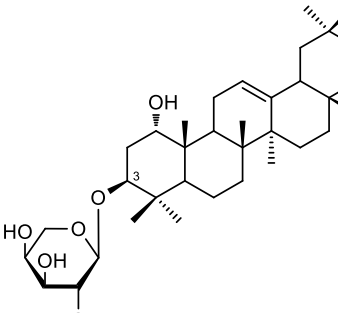
Isocucurbitacin D

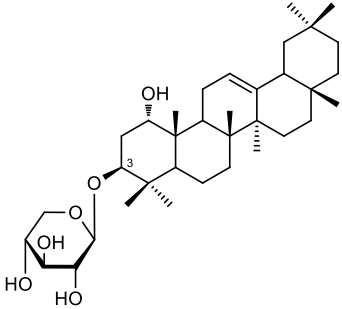
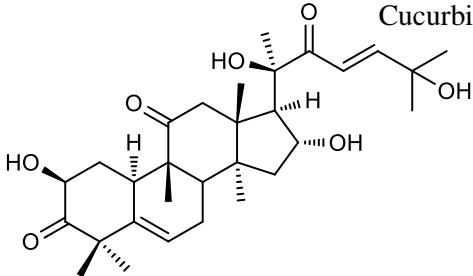
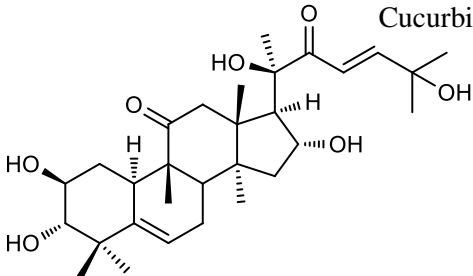


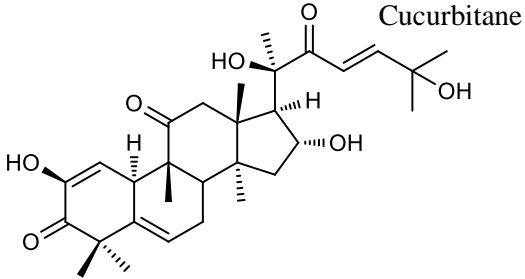
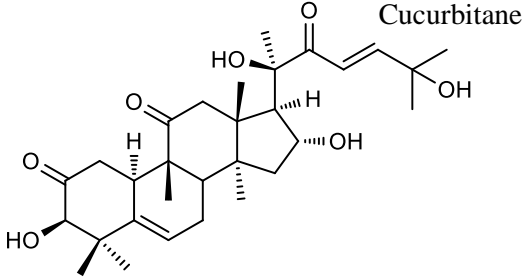
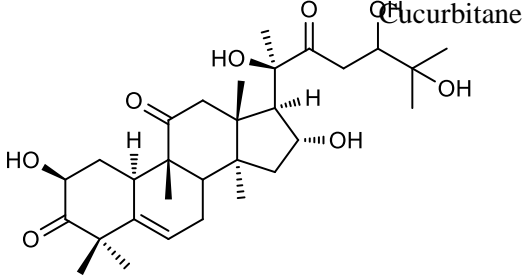
Cucurbitacin H

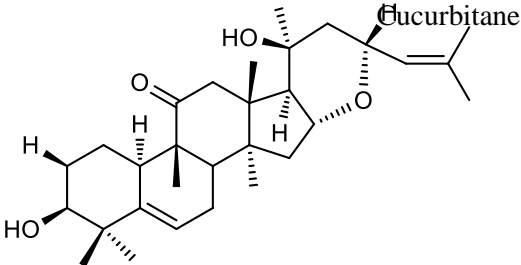
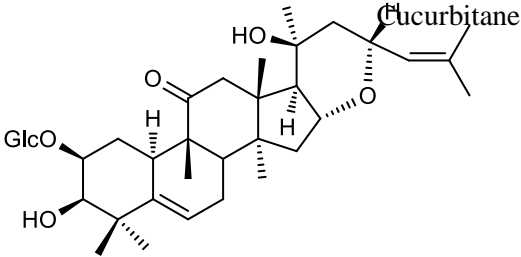
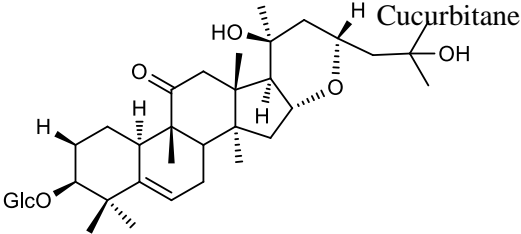
Figure S9: The isolated compounds from *E. hainanensis* in Vietnam

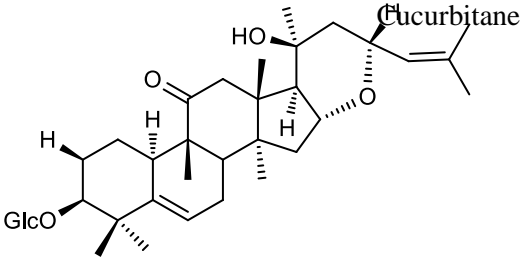
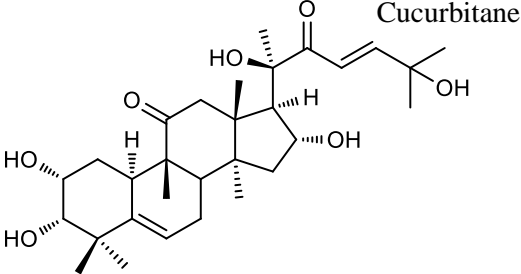
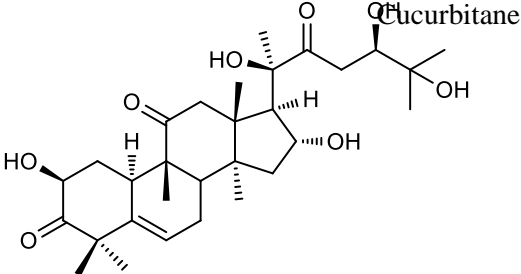
Table S1: The reported triterpenoids from the genus *Elaeocarpus* based on The Dictionary of Natural Products (2019) and this paper

No	Compound name, nomenclature	Structure	Triterpene skeleton/classification	<i>Elaeocarpus</i> species	Reference and note
1	1 α -hydroxy-olean-11-oxo-12-en-3- <i>O</i> - β -L-arabinopyranoside		Oleanane	<i>E. hainanensis</i>	The new compound (1) reported in this paper
2	1 α -Hydroxy-olean-12-en-3- <i>O</i> - β -L-arabinopyranoside		Oleanane	<i>E. hainanensis</i>	[3]

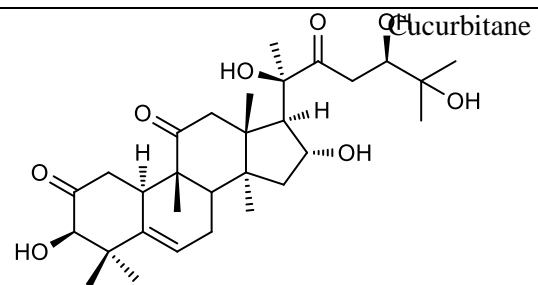
3	1 α -Hydroxy-olean-12-en-3-O- β -D-xylopyranoside		Oleanane	<i>E. hainanensis</i>	[3]
4	Cucurbitacin D		Cucurbitane	<i>E. hainanensis</i>	[3], [6]
5	Cucurbitacin F		Cucurbitane	<i>E. hainanensis</i> , <i>E. dolichostylis</i>	[3], [6]

6	Cucurbitacin I	 <p>The structure shows a complex polycyclic core with a decalin-like system fused to a six-membered ring containing a ketone and a hydroxyl group. A side chain is attached to the decalin system, featuring a carboxylic acid group, a hydroxyl group, and a terminal isopropenyl group. The label 'Cucurbitane' is placed above the side chain.</p>	<i>E. hainanensis</i>	[3], [6]
7	Isocucurbitacin D	 <p>The structure is similar to Cucurbitacin I but with a different stereochemistry at the hydroxyl group on the side chain. The label 'Cucurbitane' is placed above the side chain.</p>	<i>E. hainanensis</i>	[3]
8	Cucurbitacin H	 <p>The structure is similar to Cucurbitacin I but with a different stereochemistry at the hydroxyl group on the side chain. The label 'Cucurbitane' is placed above the side chain.</p>	<i>E. hainanensis</i>	[3]

9	16 α ,23 α -epoxy-3 β ,20 β -dihydroxy-10 α H,23 β H-cucurbita-5,24-dien-11-one		<i>E. hainanensis</i>	[6]
10	16 α ,23 α -epoxy-3 β ,20 β -dihydroxy-10 α H,23 β H-cucurbita-5,24-dien-11-one 2- <i>O</i> - β -D-glucopyranoside		<i>E. hainanensis</i>	[6]
11	16 α ,23 α -epoxy-3 β ,20 β ,25-trihydroxy-10 α H,23 β H-cucurbita-5-ene-11-one 3- <i>O</i> - β -D-glucopyranoside		<i>E. hainanensis</i>	[6]

12	16 α ,23 α -epoxy-3 β ,20 β -dihydroxy-10 α H,23 β H-cucurbita-5,24-dien-11-one 3-O- β -D-glucopyranoside		<i>E. hainanensis</i>	[6]
13	Cucurbitacin O		<i>E. hainanensis</i>	[6]
14	Cucurbitacin G		<i>E. hainanensis</i>	[6]

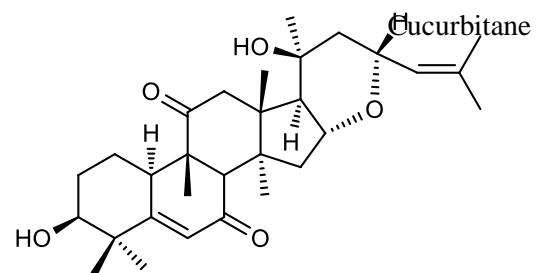
15 3-*epi*-isocucurbitacin G



E. hainanensis

[6]

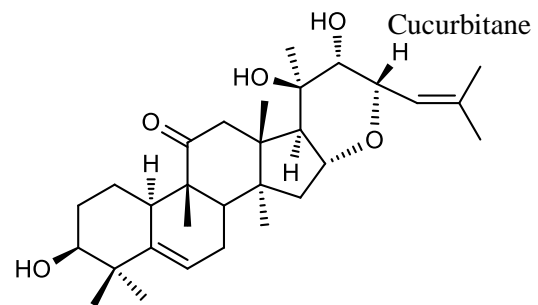
16 Elaeocarpucin H



E. chinensis

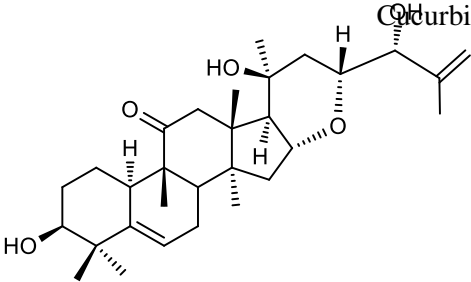
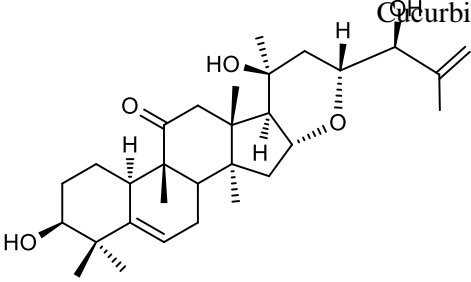
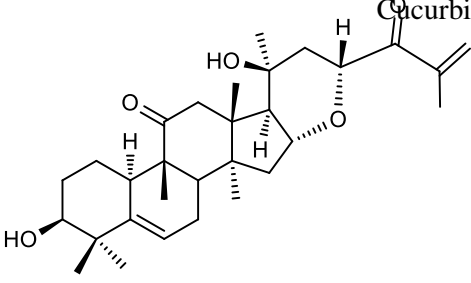
[5]

17 Elaeocarpucin G

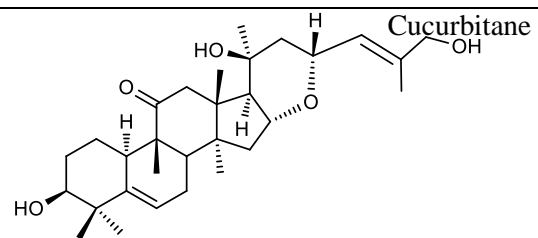


E. chinensis

[5]

18	Elaeocarpin B		<i>E. chinensis</i>	[5]
19	Elaeocarpin A		<i>E. chinensis</i>	[5]
20	Elaeocarpin D		<i>E. chinensis</i>	[5]

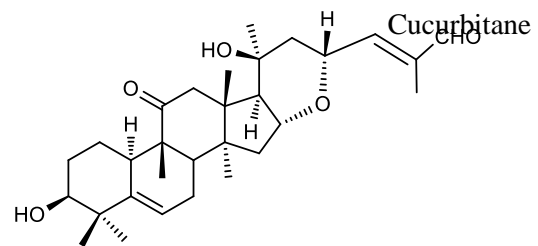
21 Elaeocarpucin C



E. chinensis

[5]

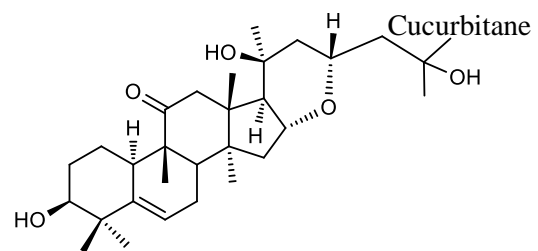
22 Elaeocarpucin E



E. chinensis

[5]

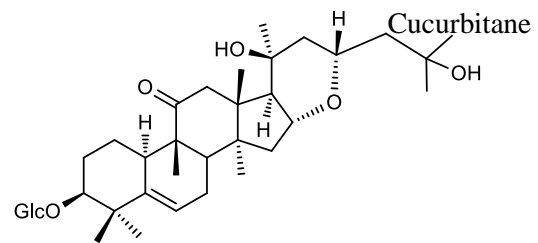
23 Elaeocarpucin F



E. chinensis

[5]

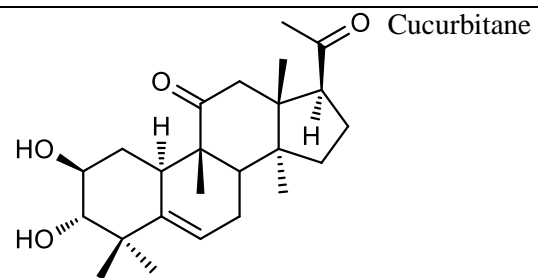
24 Elaeocarpucin F 3-O- β -D-glucopyranoside



E. chinensis

[5]

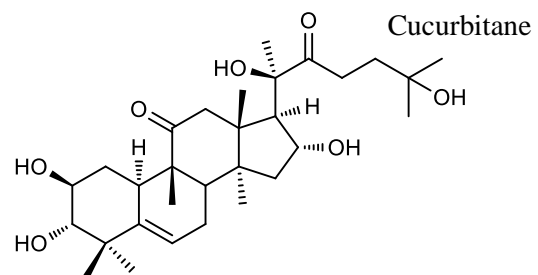
25 Hexanorcucurbitacin F



E. dolichostylus

[17]

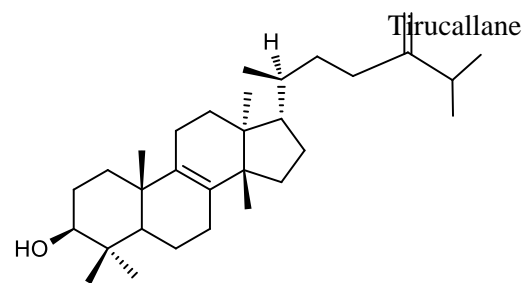
26 23,24-Dihydrocucurbitacin F



E. dolichostylus

[17]

27 Euphorbol



E. floribundus

[16]