

Caribenols A and B, Sea Whip-Derived Norditerpenes with Novel Tricarbocyclic Skeletons

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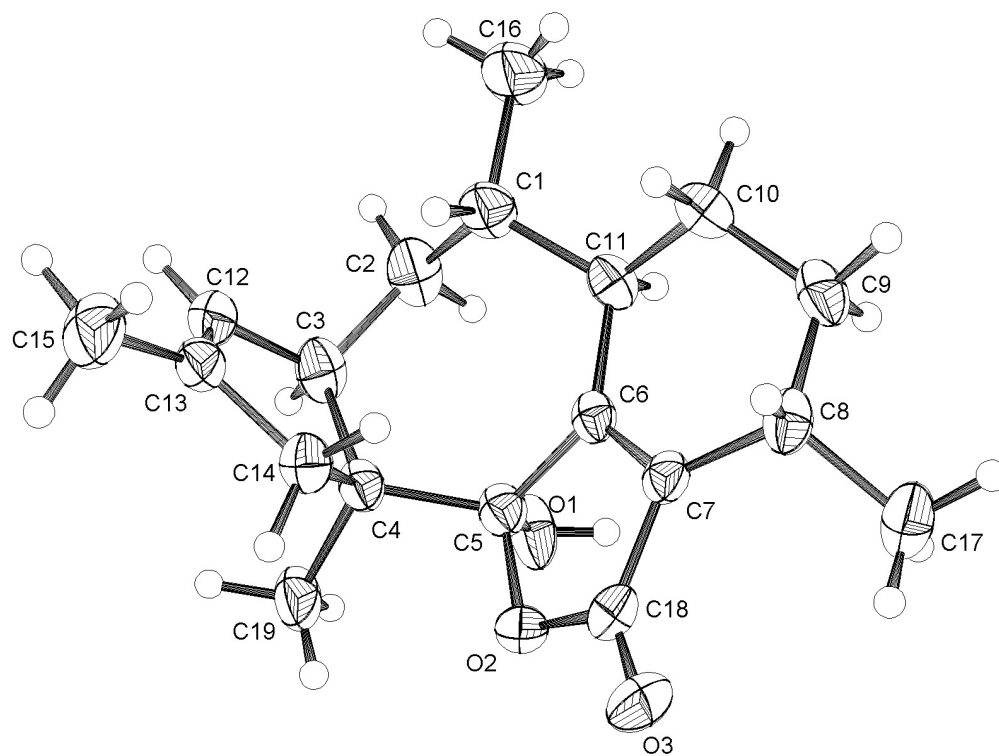
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HMBC Spectrum of Caribenol B in CDCl_3 (S14)

NOESY Spectrum of Caribenol B in CDCl_3 (S15)

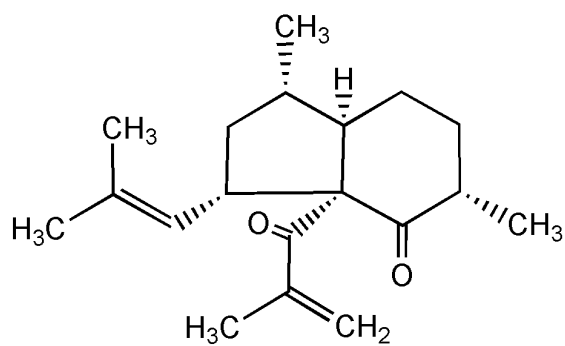
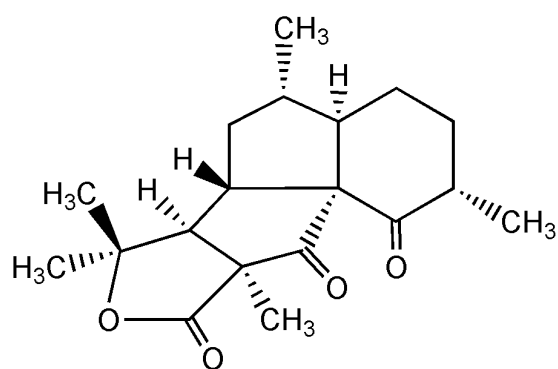
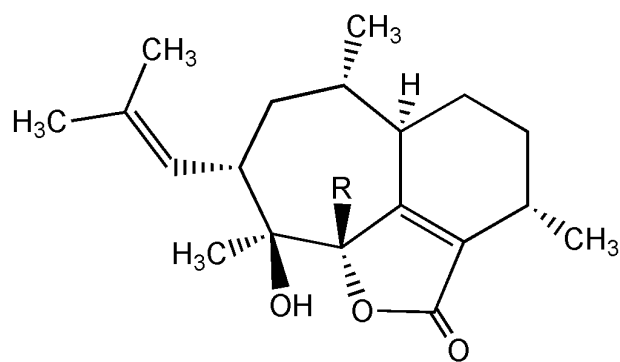
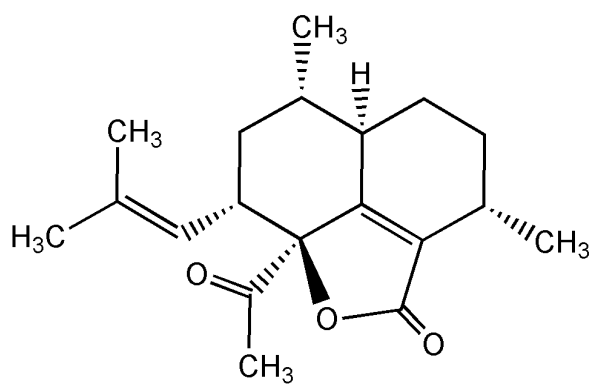
S2

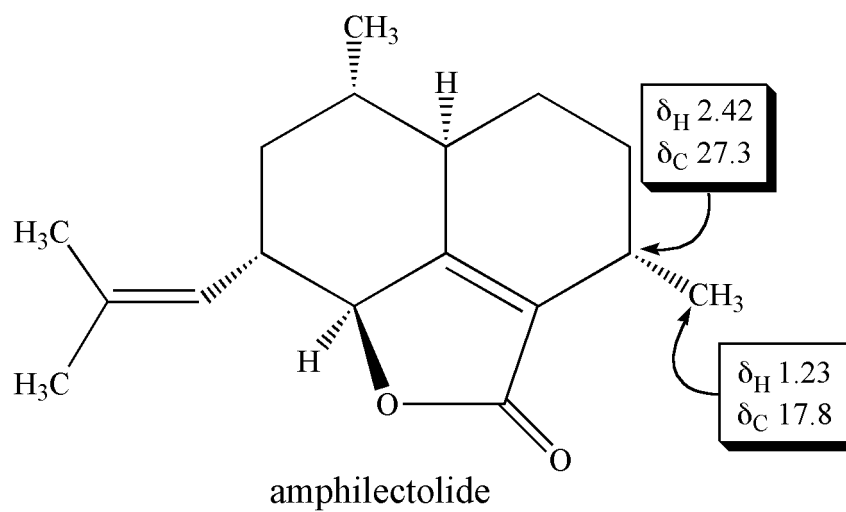
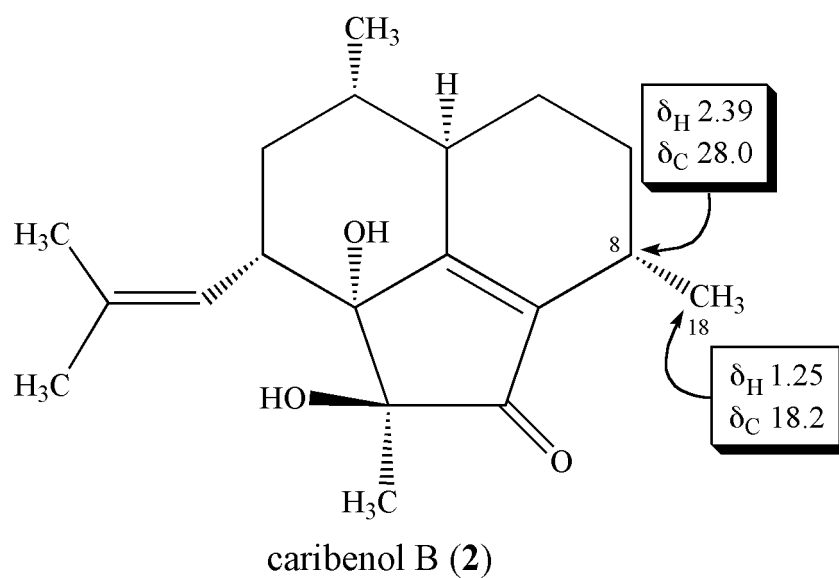


ORTEP drawing for Caribenol A

Crossover Products Isolated from the Two *Pseudopterogorgia elisabethae* Chemotypes.

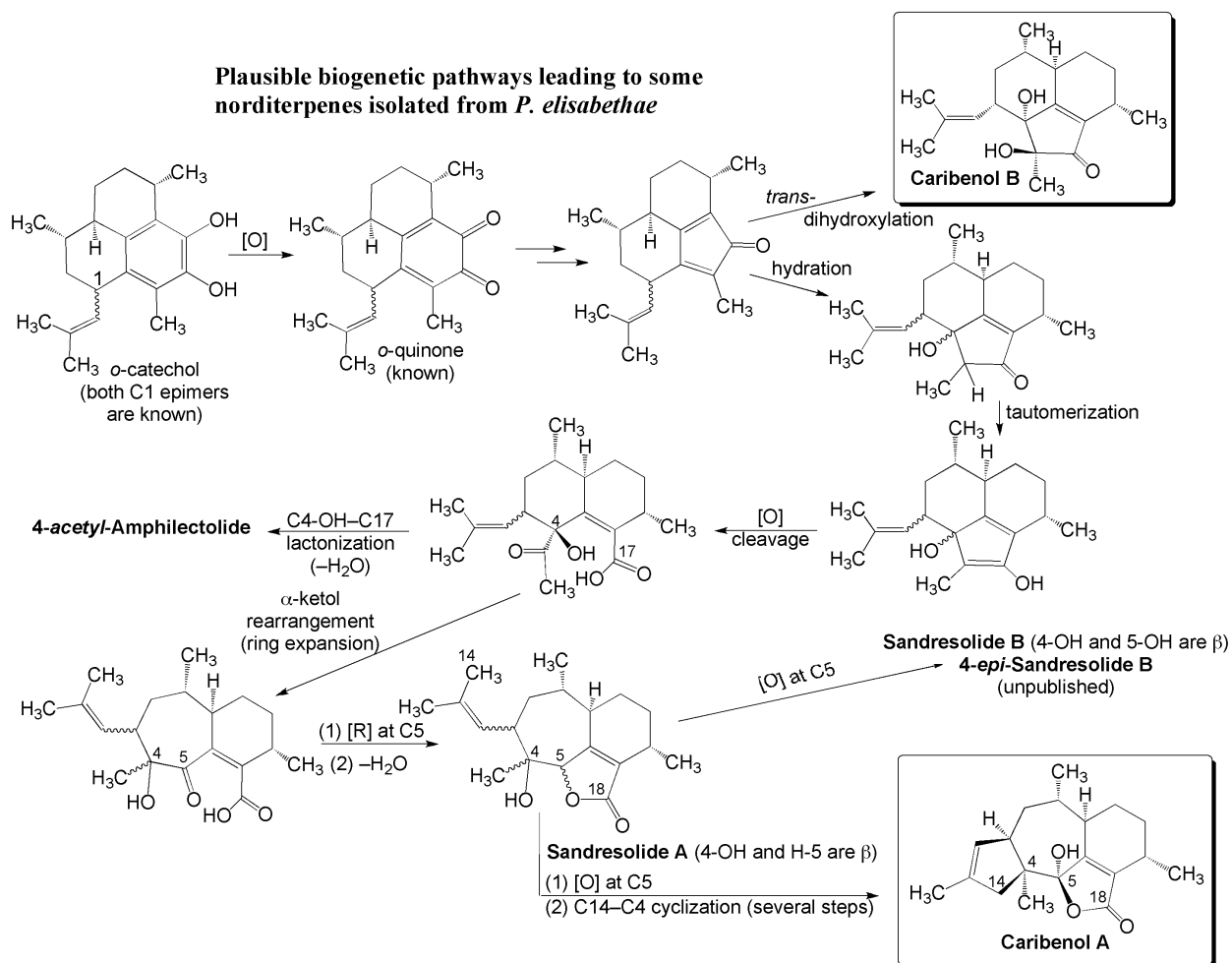
Chemotype I (Old Providence Island) was characterized by its massive production of pseudopterოსins. Eleven new members of this profuse family of anti-inflammatory diterpene-glycosides were reported by us in 2004.² However, trace amounts of other known compounds previously isolated from chemotype II (San Andrés Island) were also detected within the extracts of chemotype I. The purification of a medium polar fraction of the hexane extract of *P. elisabethae* (chemotype I) by successive size exclusion chromatography (Bio-Beads® SX-3 in toluene), column chromatography (15 g silica gel in 8:2 chloroform-hexane), and HPLC (Polar-Bonded Cyano column in 97:3 hexane-isopropanol) led to the isolation of **elisapterosin A** (4.3 mg), **elisabanolide** (2.0 mg), and **cumbiasin C** (2.1 mg). Another compound that appears to be biogenetically related to other compounds isolated from chemotype II is **ileabethoxazole**. The latter metabolite is based on the known ileabethane carbon skeleton and contains the rare benzoxazole moiety (first detected from compounds isolated from chemotype II, namely, **ileabethane** and **pseudopteroxazole**). *P. elisabethae* from San Andrés Island is characterized by the presence of a complex array of secondary metabolites identified as diterpenoids based on a series of novel carbon skeletons that have been reported over the last decade.³ Some of these families of compounds include the elisabethanes, elisabanes, colombianes, sandresanes, cumbianes, and ileabethanes. It is rather curious that only two *seco*-pseudopterოსins were isolated (in trace amounts) from the study of *P. elisabethae* colonies from San Andrés Island (chemotype II).

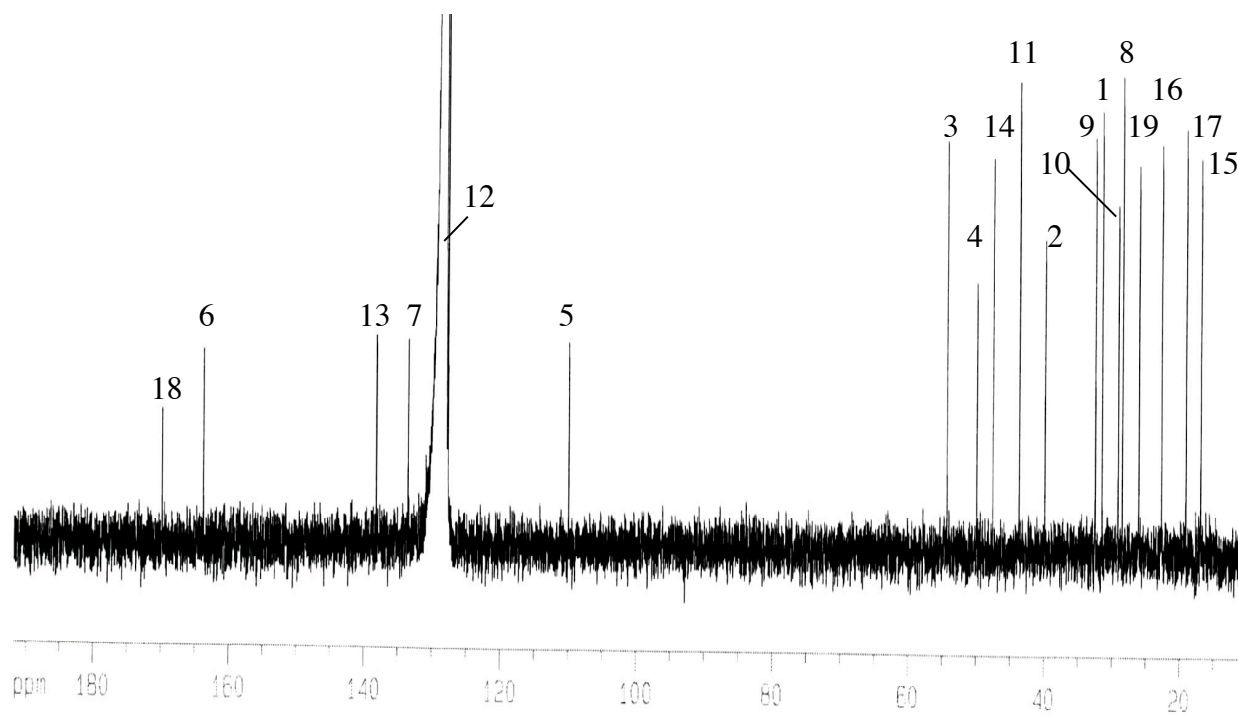
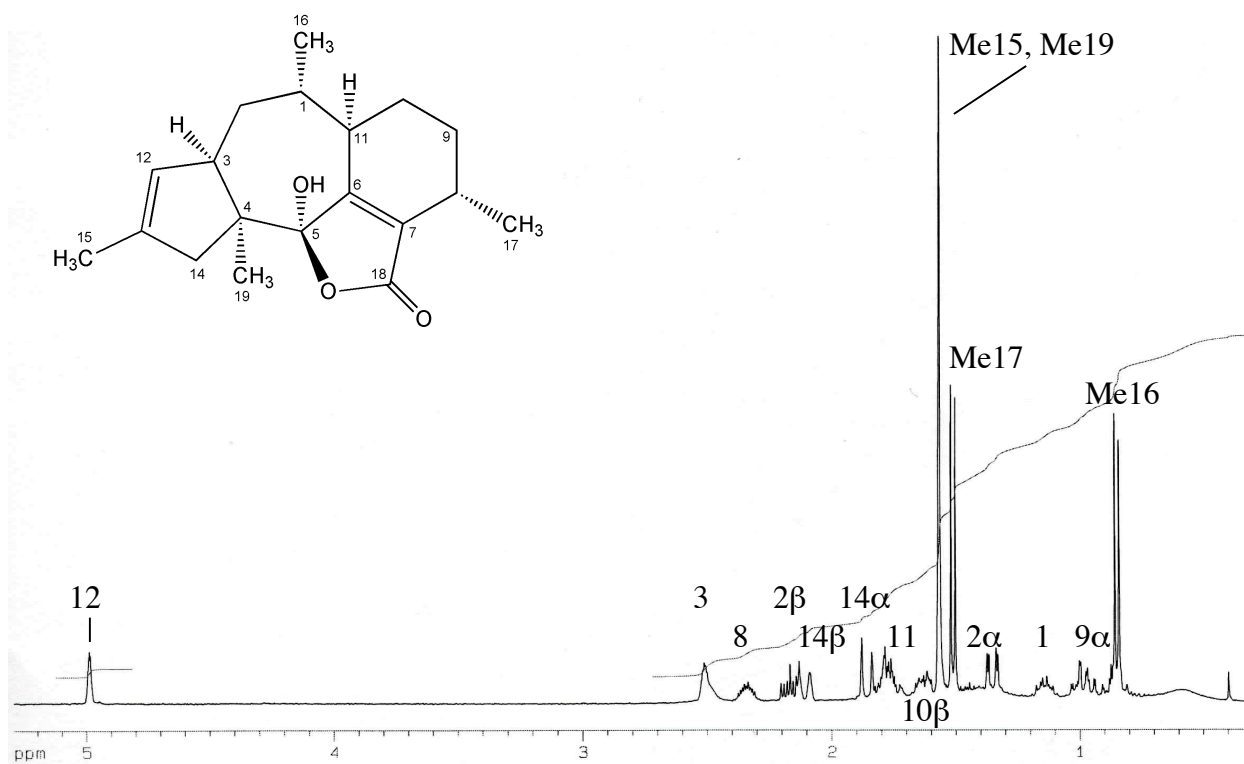
Selected Norditerpenes Previously Isolated from *Pseudopterogorgia elisabethae***Elisabethin B****Elisabanolide****Sandresolide A:** R = H
Sandresolide B: R = OH**4-acetyl-Amphilectolide**

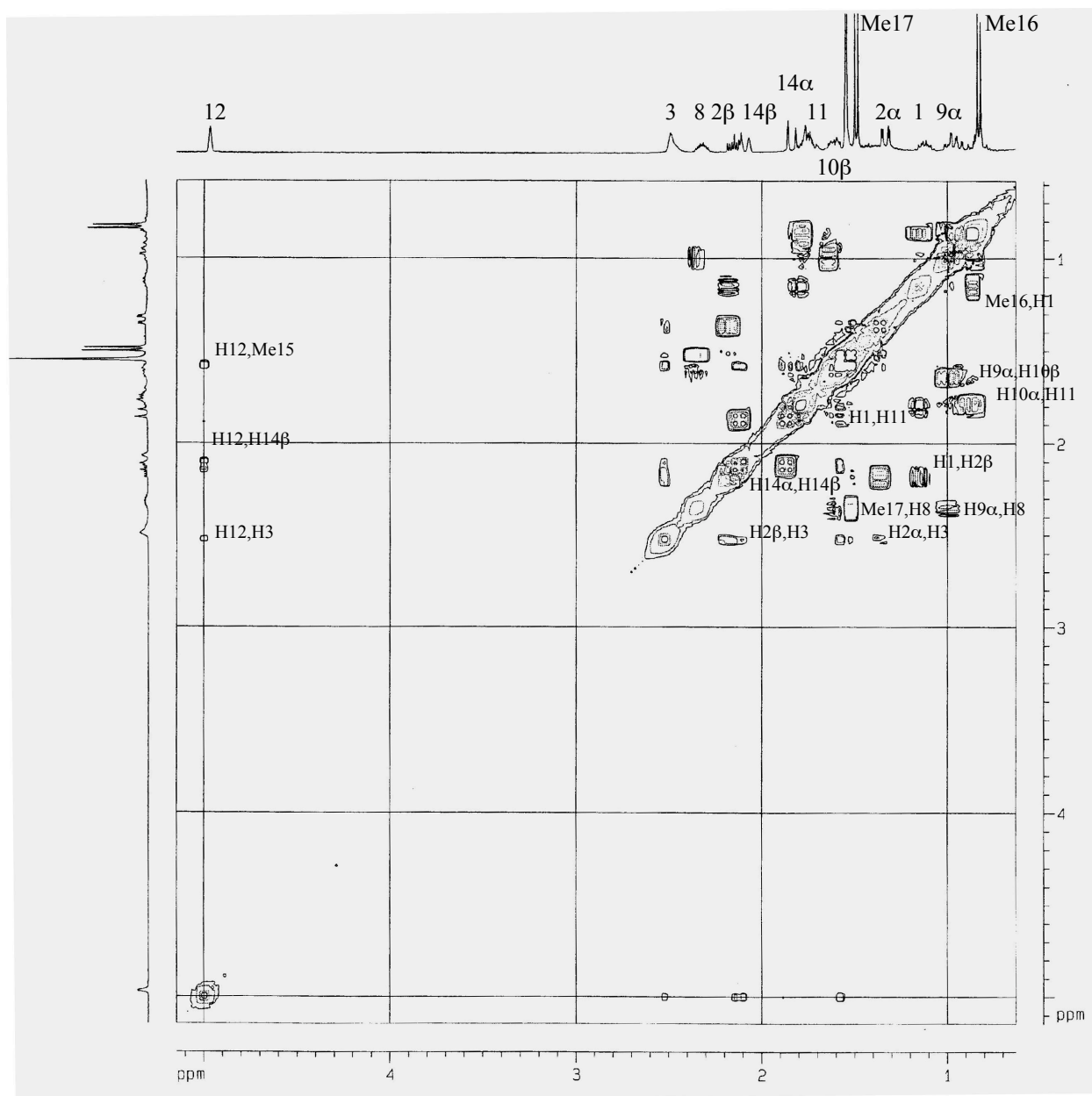
Key ^1H and ^{13}C NMR Chemical Shifts Comparison of Caribenol B (2) and Amphilectolide*

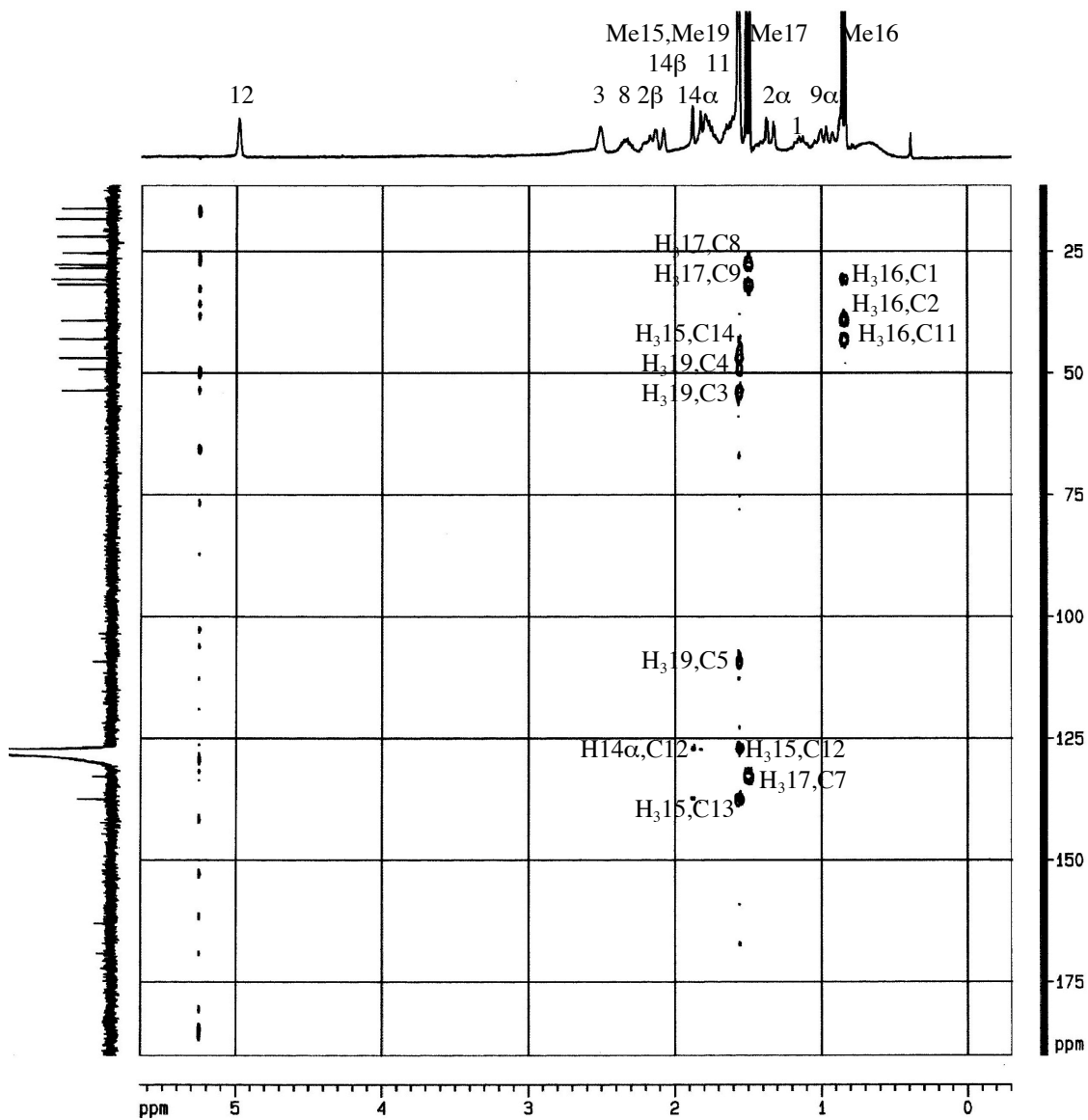
* The NMR data for the two metabolites shown were acquired in CDCl_3 .

Plausible biogenetic pathways leading to some norditerpenes isolated from *P. elisabethae*

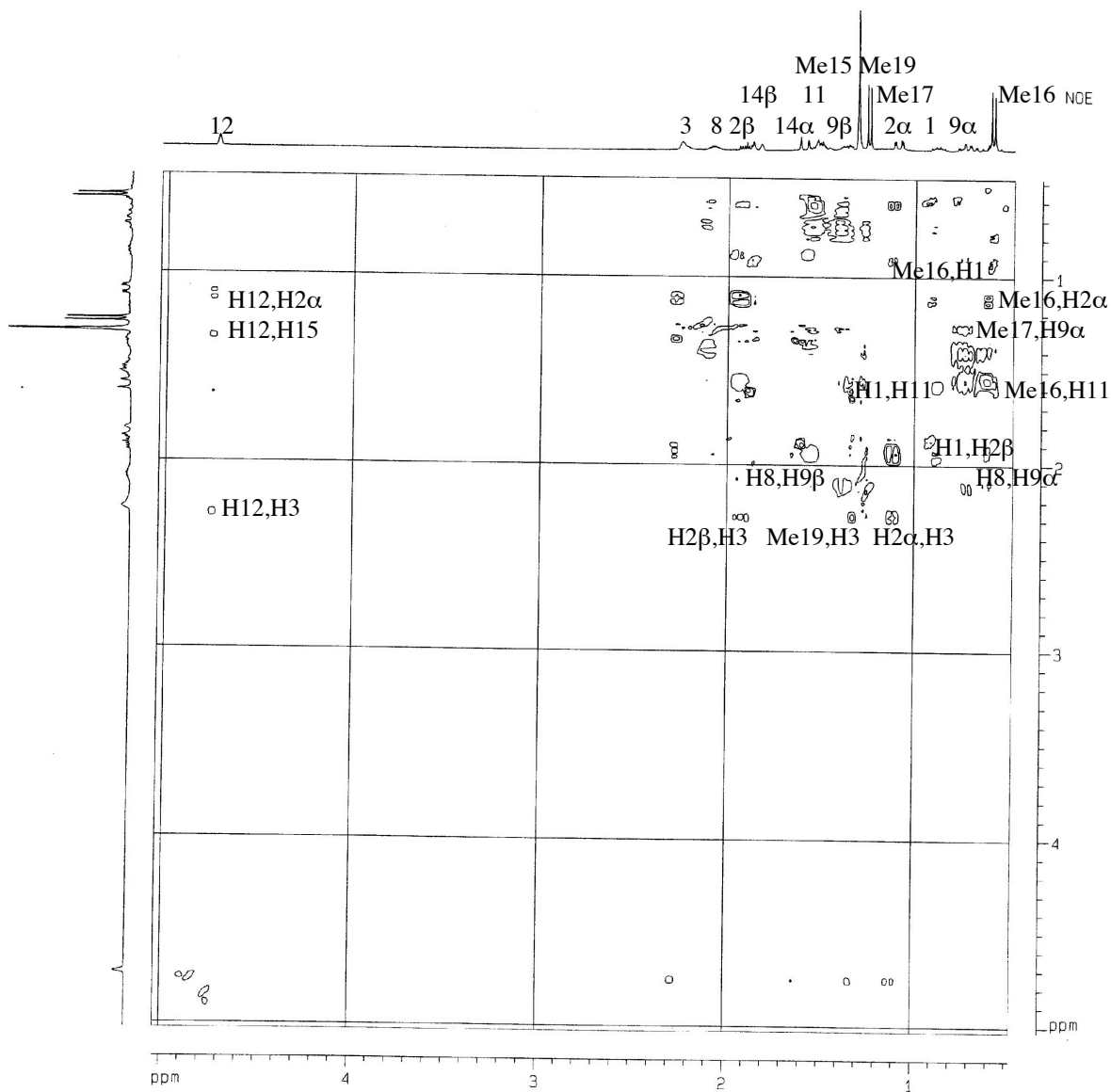


^1H and ^{13}C NMR Spectra of Caribenol A in C_6D_6 

^1H - ^1H COSY Spectrum of Caribenol A in C_6D_6 

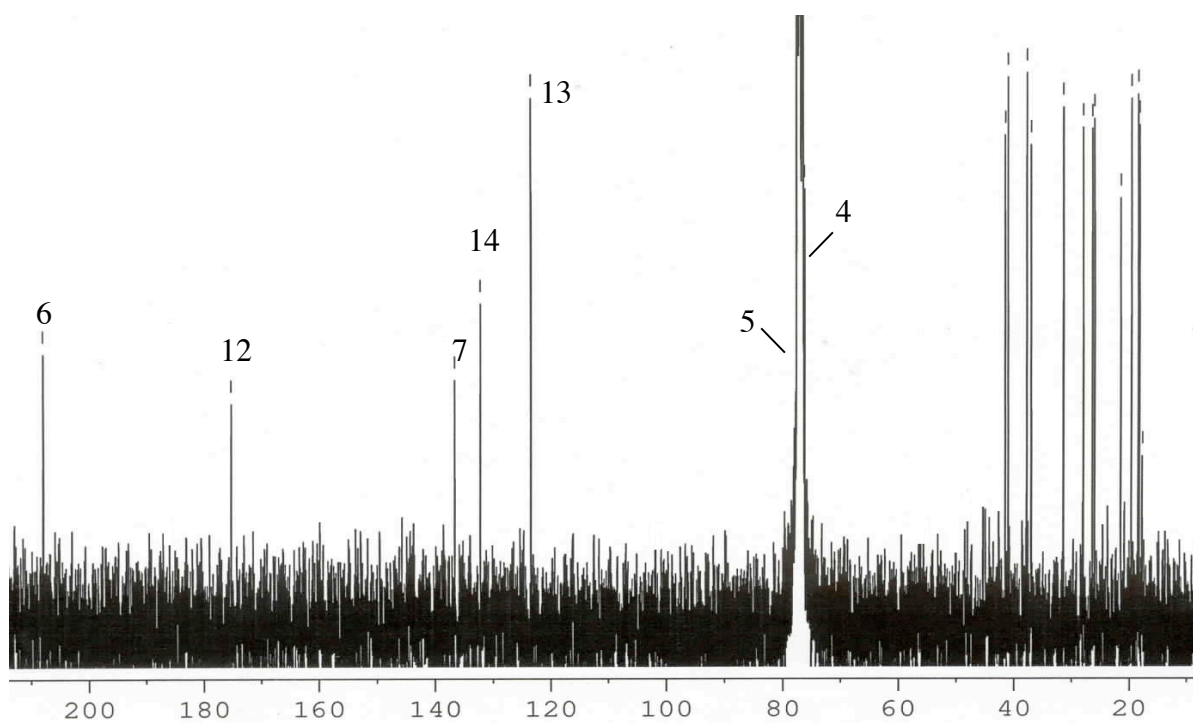
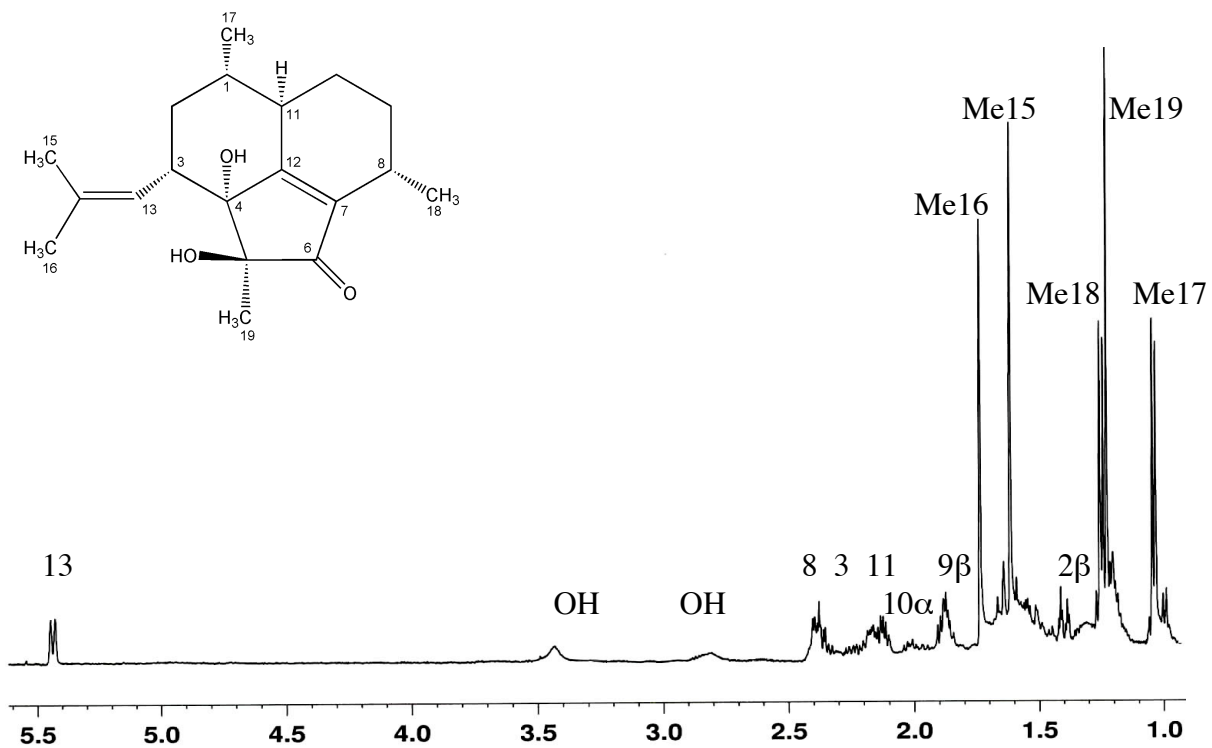
HMBC Spectrum of Caribenol A in C_6D_6 

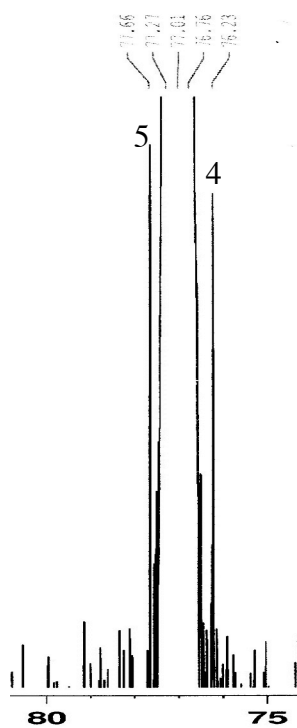
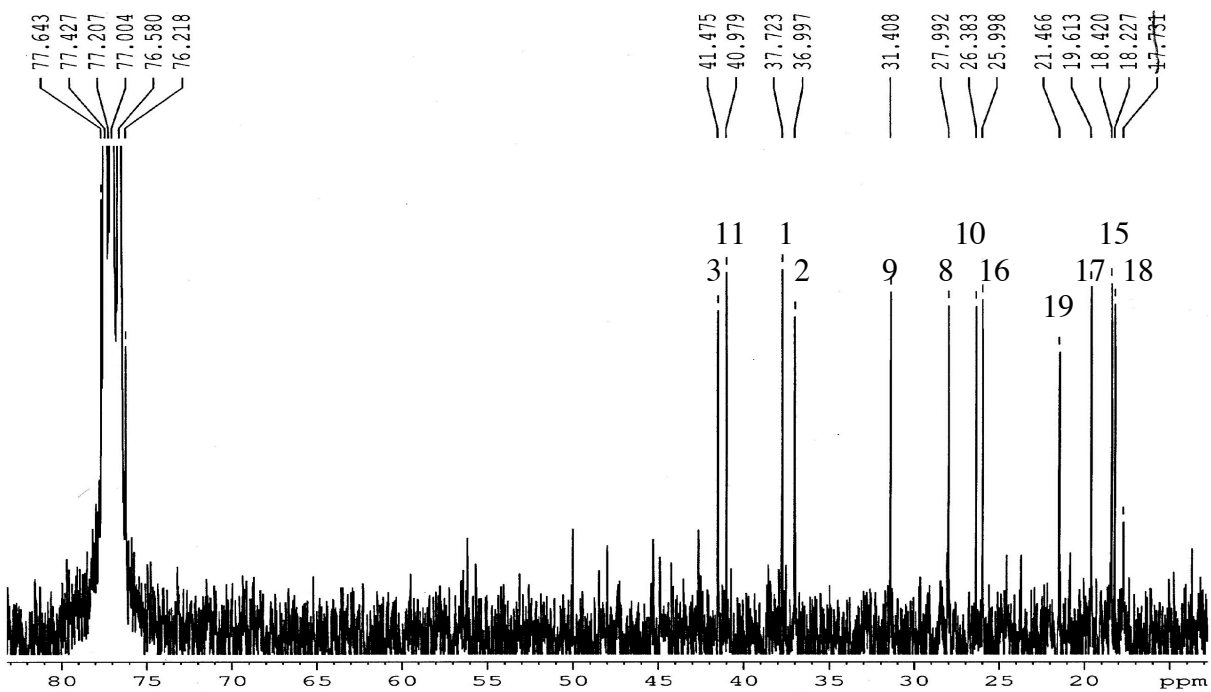
NOESY Spectrum of Caribenol A in C₆D₆



S11

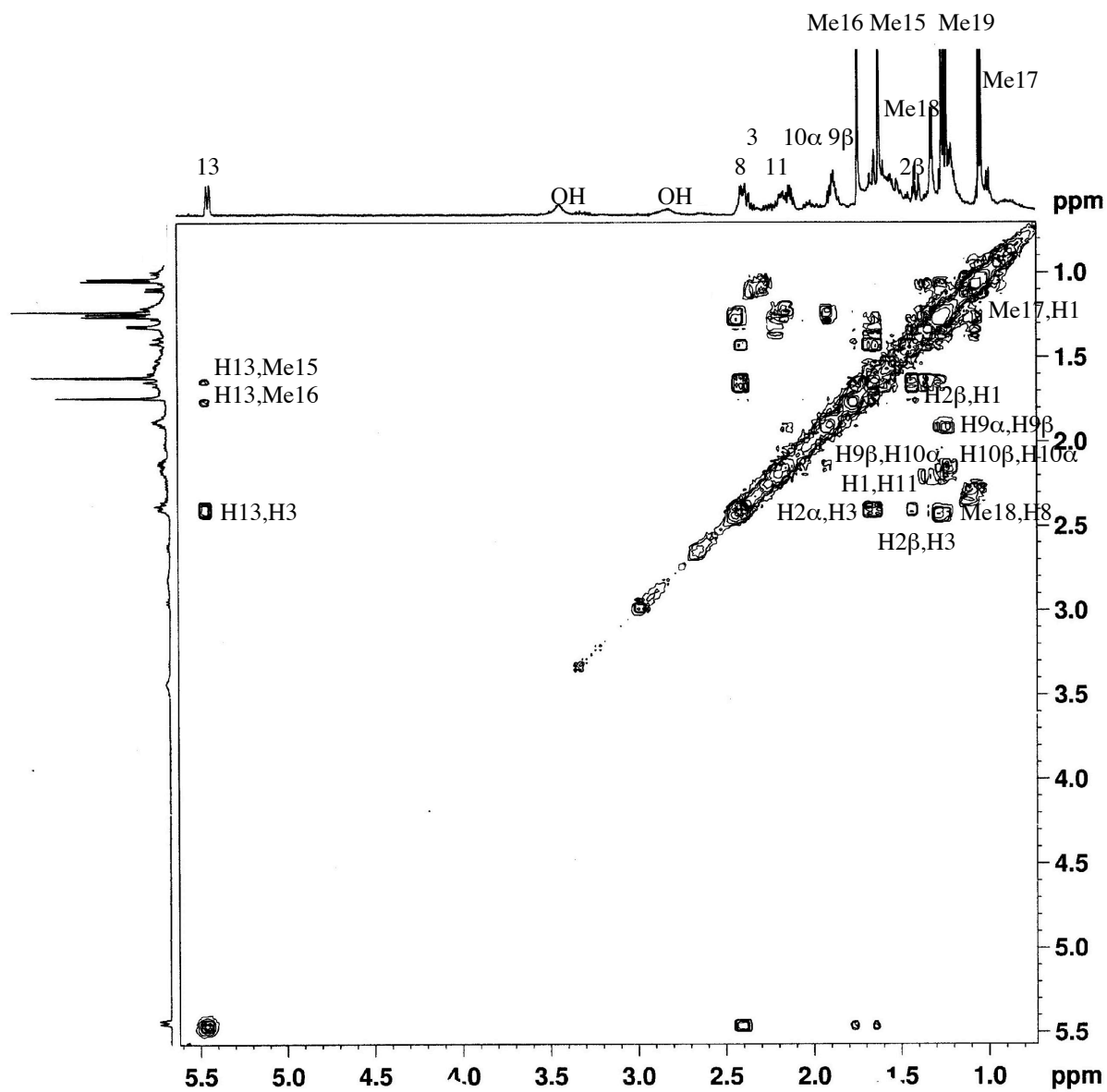
^1H and ^{13}C NMR Spectra of Caribenol B in CDCl_3

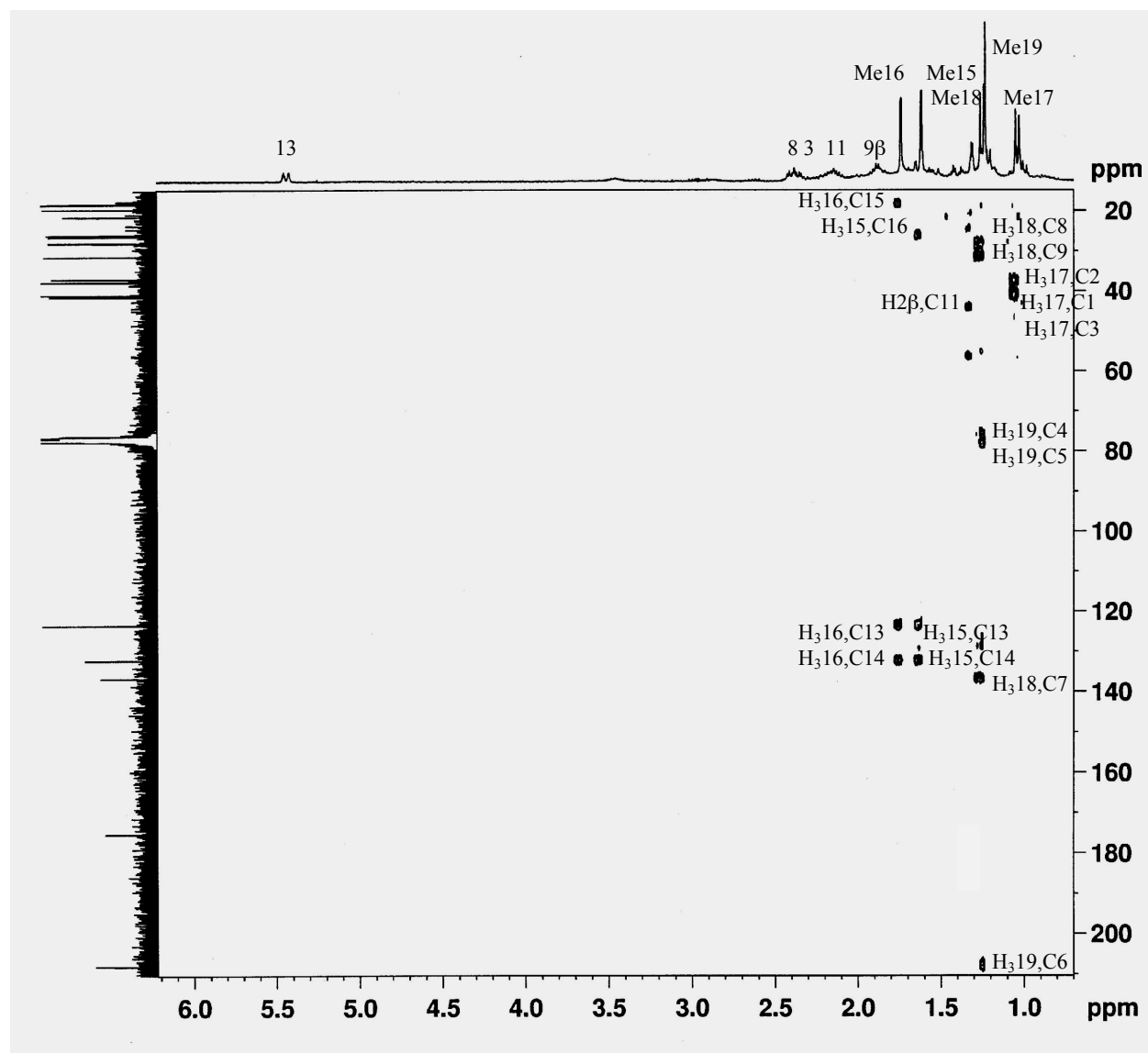


Expansions of the ^{13}C NMR Spectrum of Caribenol B in CDCl_3 

S13

^1H - ^1H COSY Spectrum of Caribenol B in CDCl_3



HMBC Spectrum of Caribenol B in CDCl₃

NOESY Spectrum of Caribenol B in CDCl₃