

Supplementary Information

Rodriguesic Acids, Modified Diketopiperazines from the Gastropod Mollusc *Pleurobranchus areolatus*

Fabio R. Pereira,^a Mario F. C. Santos,^a David E. Williams,^b Raymond J. Andersen,^b
Vinicius Padula,^c Antonio G. Ferreira^d and Roberto G. S. Berlinck^{*a}

^aInstituto de Química de São Carlos, Universidade de São Paulo,
CP 780, 13560-970 São Carlos-SP, Brazil

^bDepartments of Chemistry and Earth, Ocean & Atmospheric Sciences,
University of British Columbia, Vancouver, BC, V6T 1Z1, Canada

^cSNSB-Zoologische Staatssammlung München, Münchhausenstrasse 21,
81247 München, Germany and Department Biology II and GeoBio-Center,
Ludwig-Maximilians-Universität München, Germany

^dDepartamento de Química, Universidade Federal de São Carlos,
Rodovia Washington Luiz, km 235, 13565-905 São Carlos-SP, Brazil

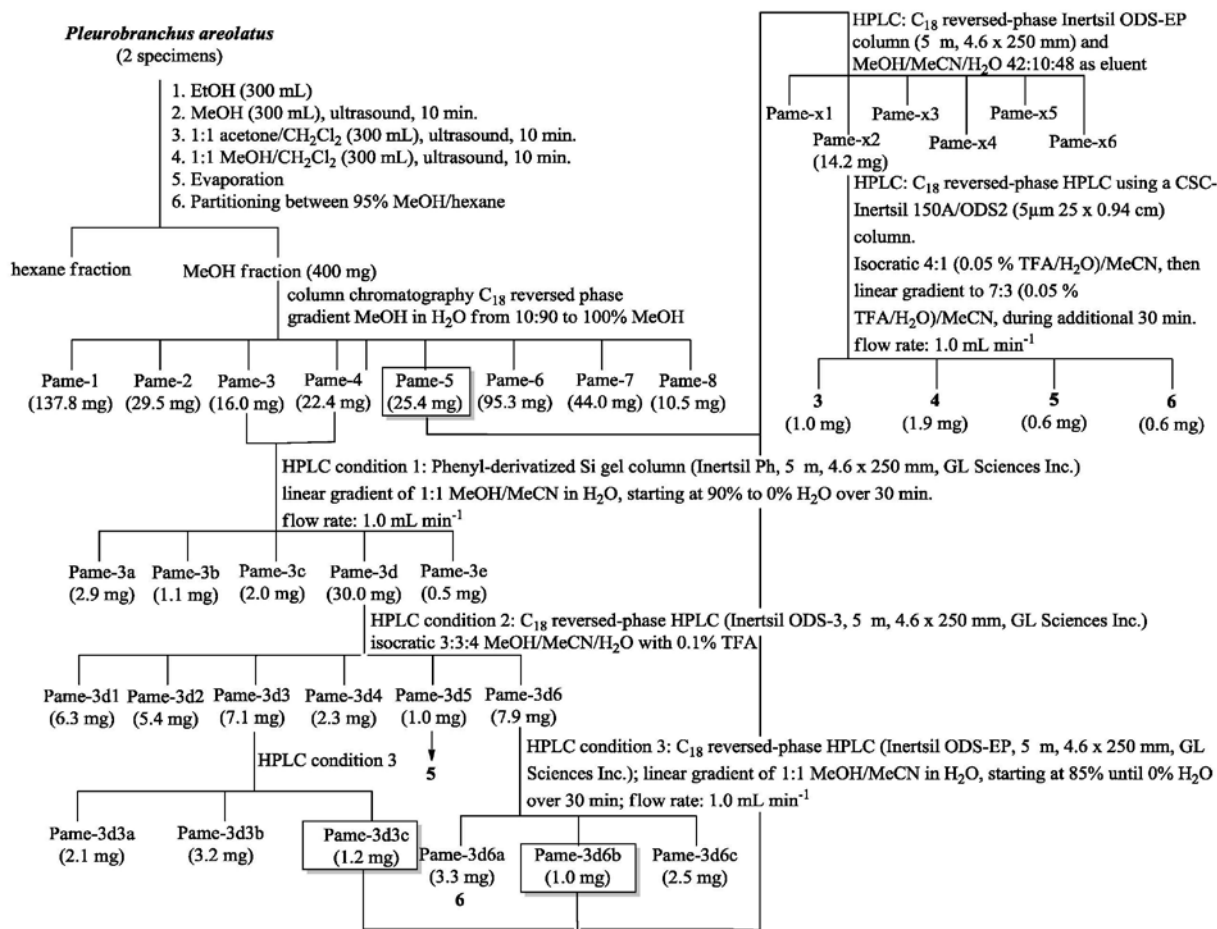


Figure S1. Separation scheme for the isolation of rodriguesic acid derivatives 3-6.

*e-mail: rgsberlinck@iqsc.usp.br

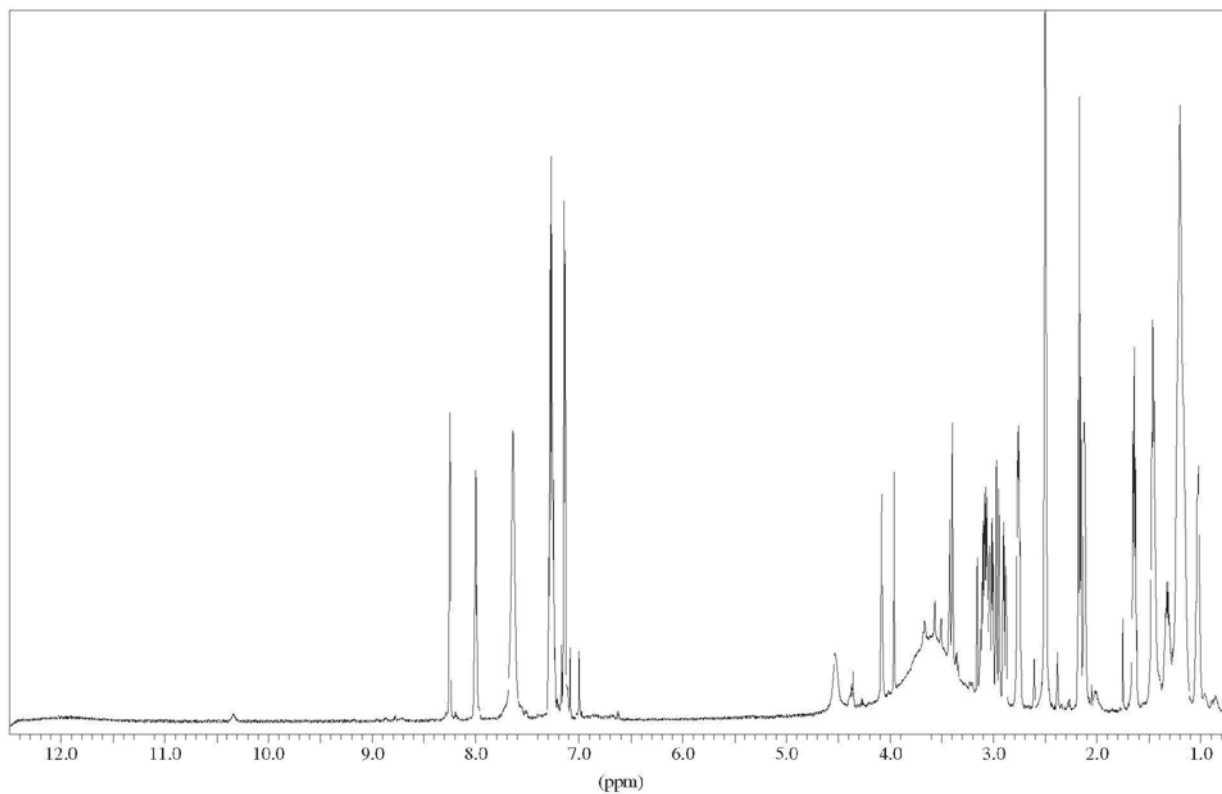


Figure S2. ¹H NMR spectrum of rodriguesic acid (**3**) in DMSO-*d*₆ at 600 MHz.

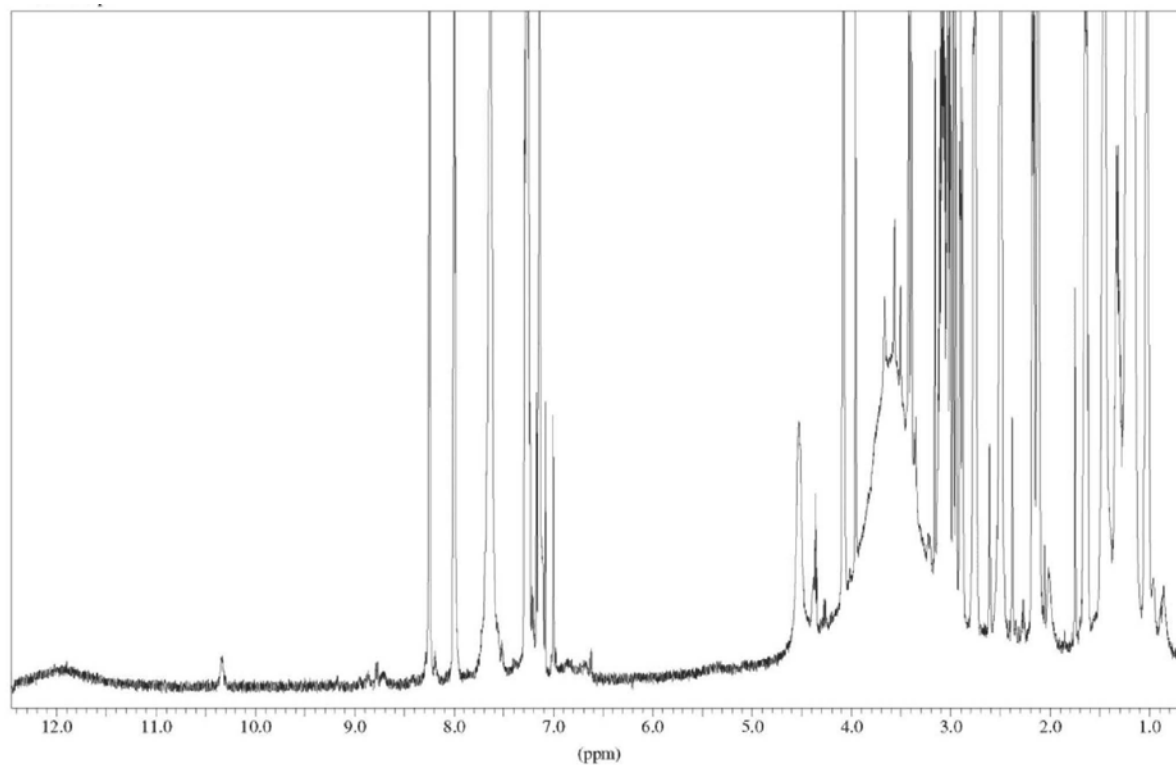


Figure S3. Expansion of the ¹H NMR spectrum of rodriguesic acid (**3**) in DMSO-*d*₆ at 600 MHz.

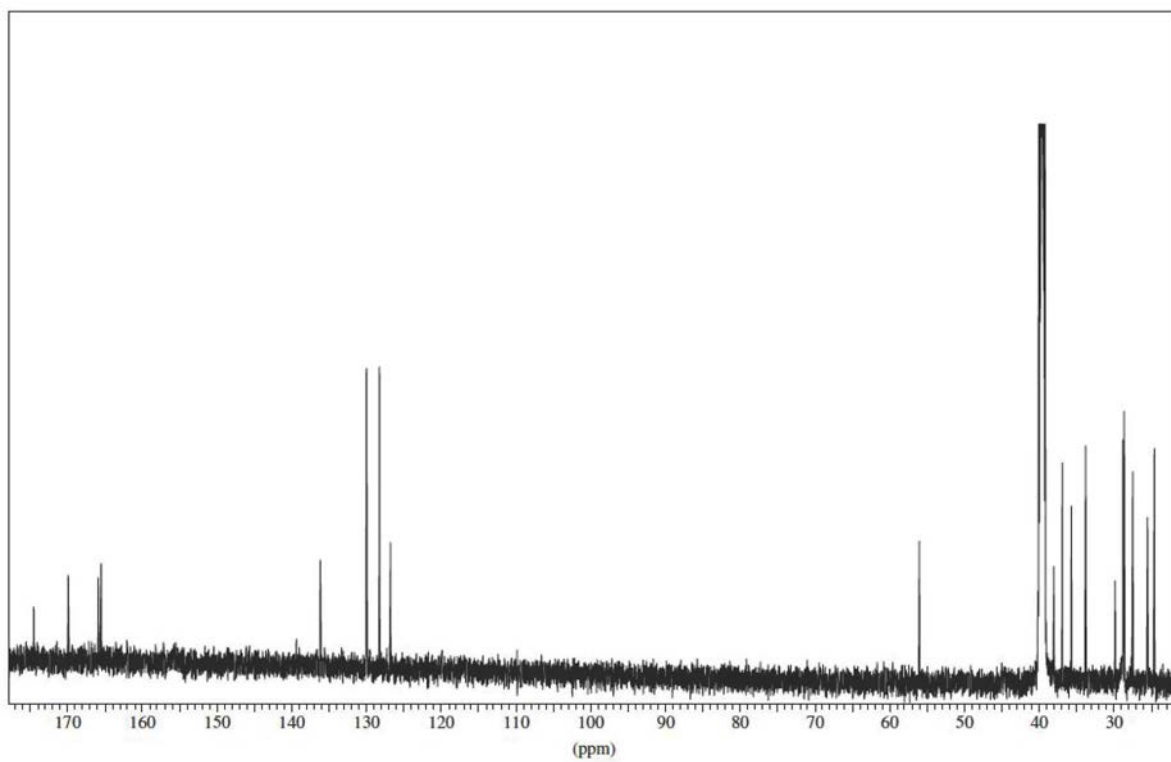


Figure S4. ^{13}C NMR spectrum of rodriguesic acid (**3**) in $\text{DMSO-}d_6$ at 150 MHz.

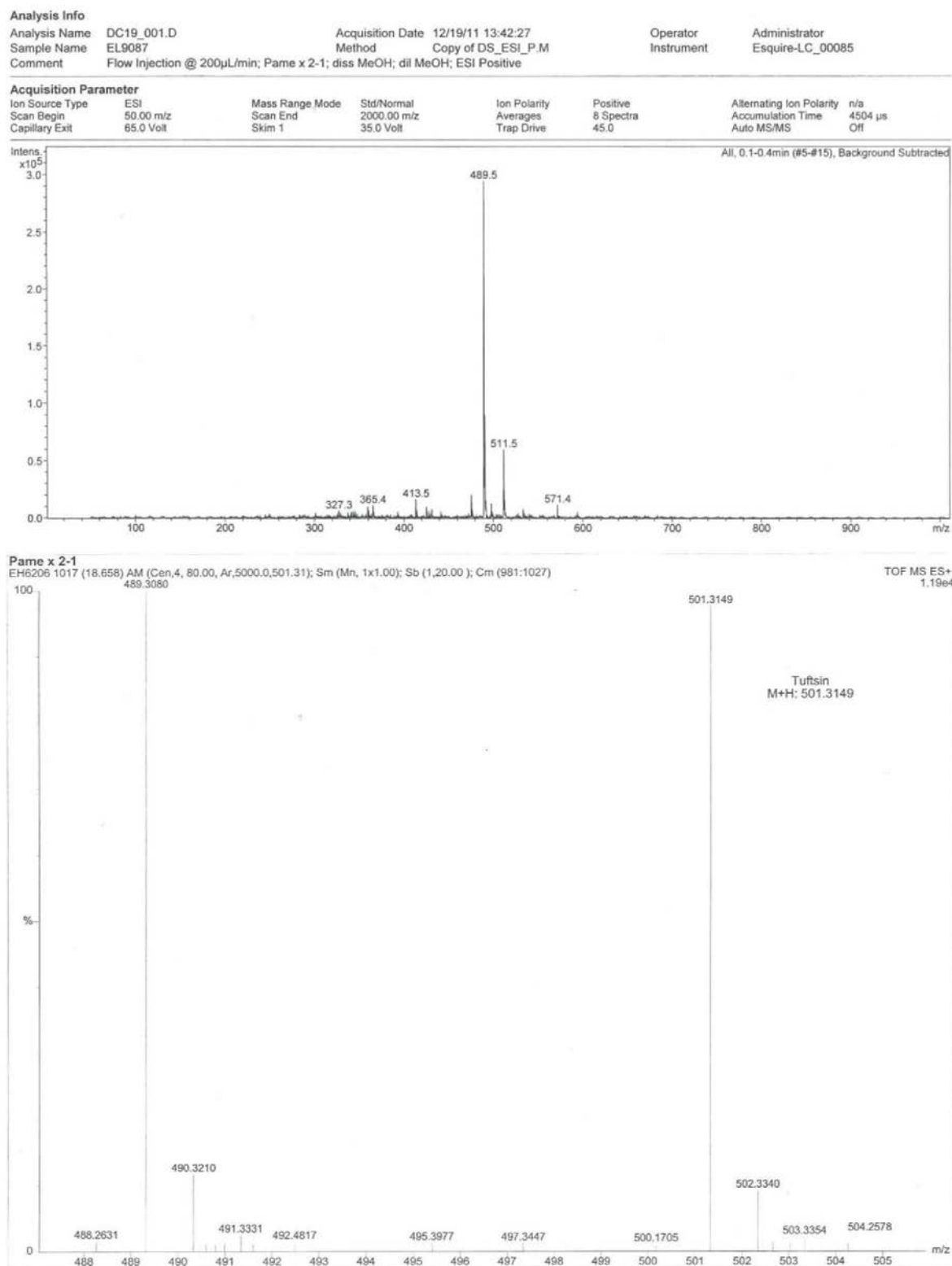


Figure S5. LR-ESI (top) and HR-ESI (bottom) mass spectra of rodriguesic acid (3).

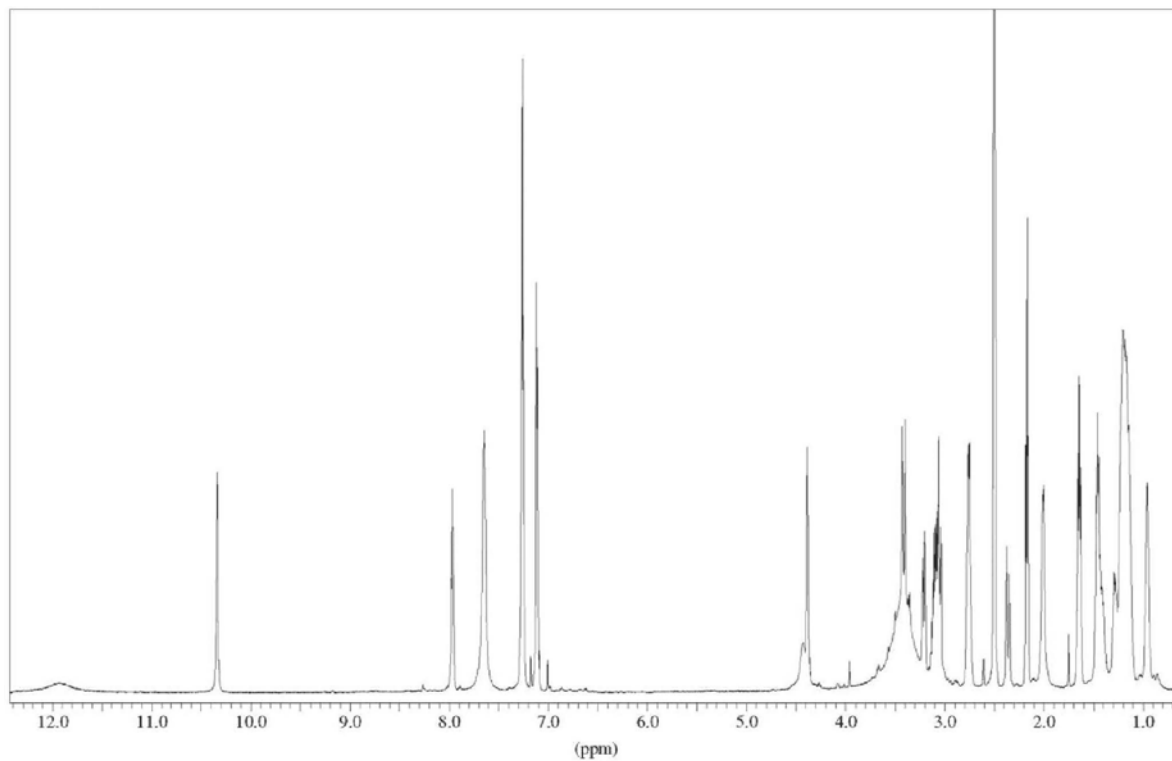


Figure S6. ¹H NMR spectrum of the rodriguesic acid hydroxamate (**4**) in DMSO-*d*₆ at 600 MHz.

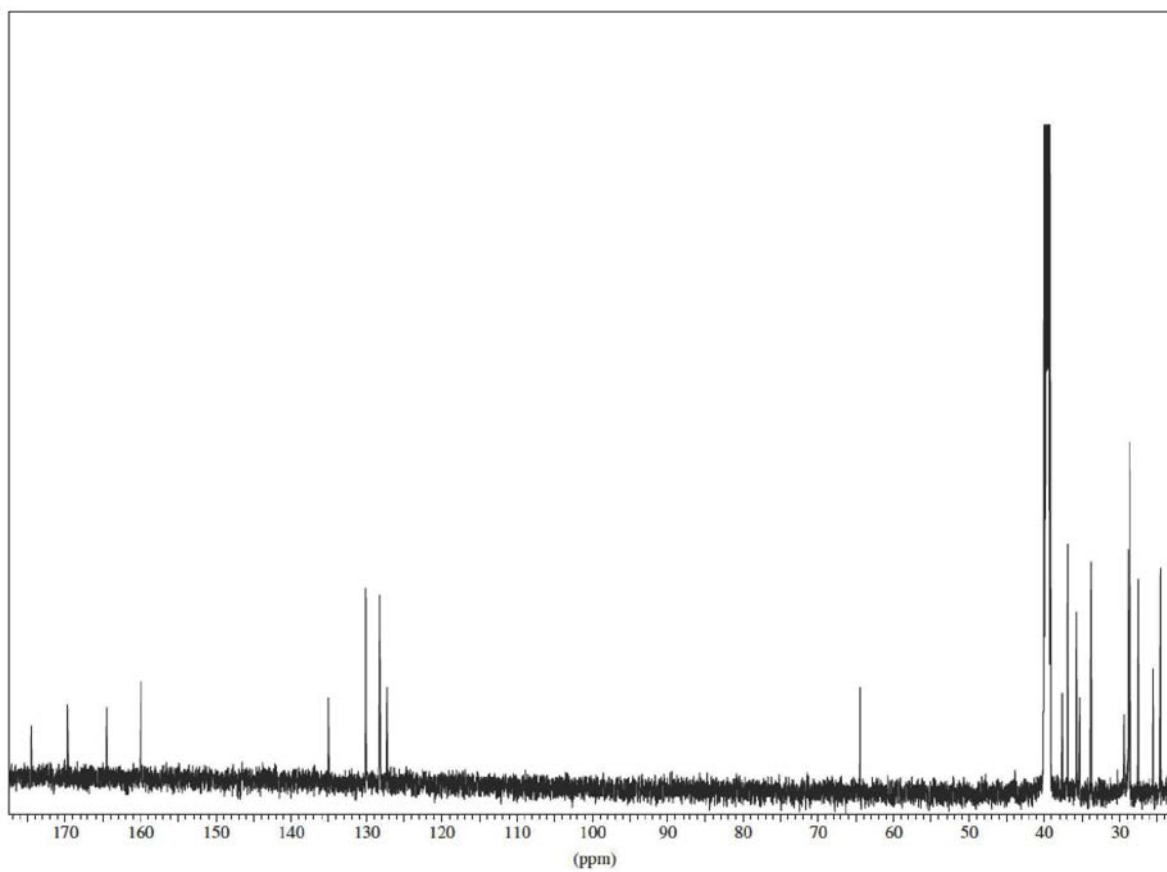


Figure S7. ¹³C NMR spectrum of the rodriguesic acid hydroxamate (**4**) in DMSO-*d*₆ at 150 MHz.

Analysis Info

Analysis Name	DC19_005.D	Acquisition Date	12/19/11 14:03:15	Operator	Administrator
Sample Name	EL9088	Method	Copy of DS_ESI_P.M	Instrument	Esquire-LC_00085
Comment	Flow Injection @ 200 μ L/min; Pame x 2-2; diss MeOH; dil MeOH; ESI Positive				

Acquisition Parameter

Ion Source Type	ESI	Mass Range Mode	Std/Normal	Ion Polarity	Positive	Alternating Ion Polarity	n/a
Scan Begin	50.00 m/z	Scan End	2000.00 m/z	Averages	8 Spectra	Accumulation Time	4335 μ s
Capillary Exit	65.0 Volt	Skim 1	35.0 Volt	Trap Drive	45.0	Auto MS/MS	Off

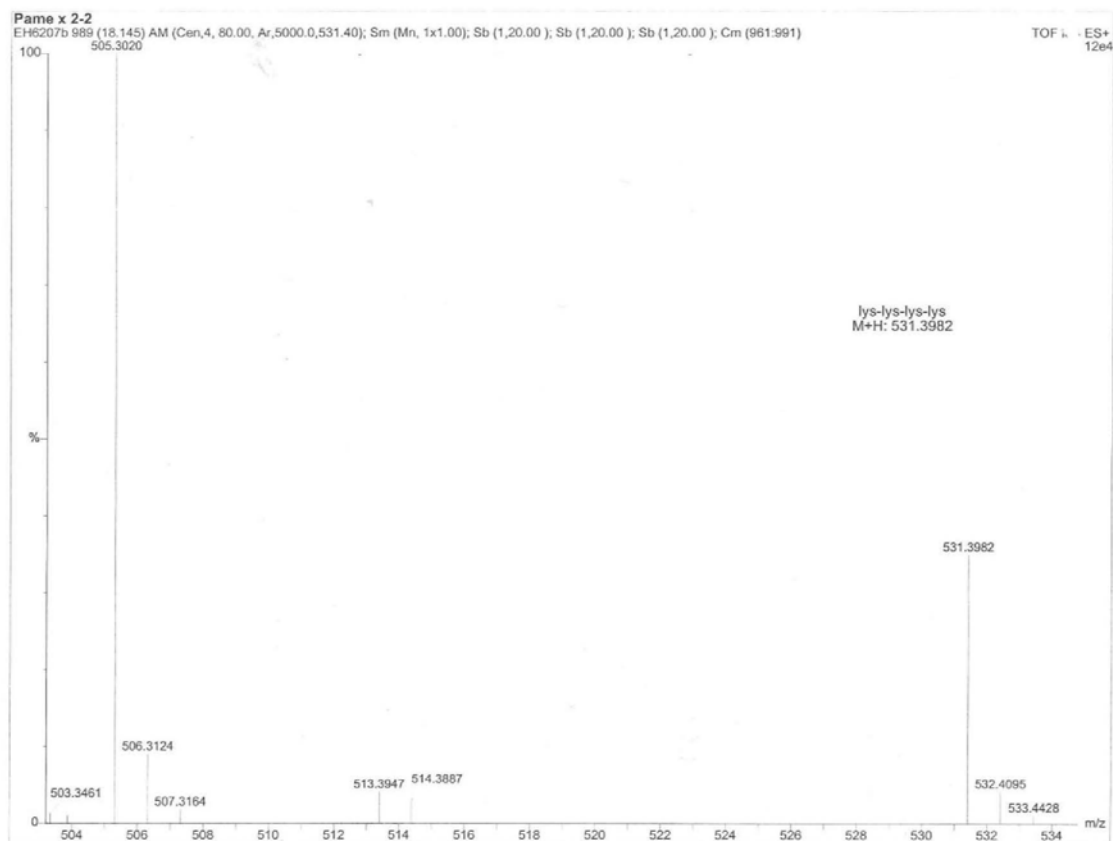
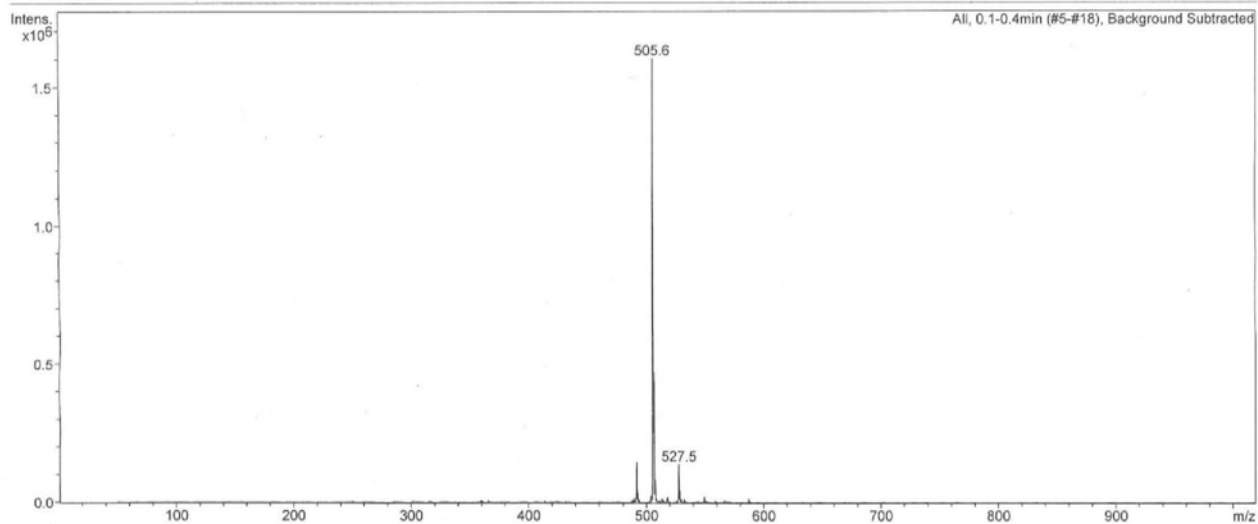


Figure S8. LR-ESI (top) and HR-ESI (bottom) mass spectra of the rodriguesic acid hydroxamate (**4**).

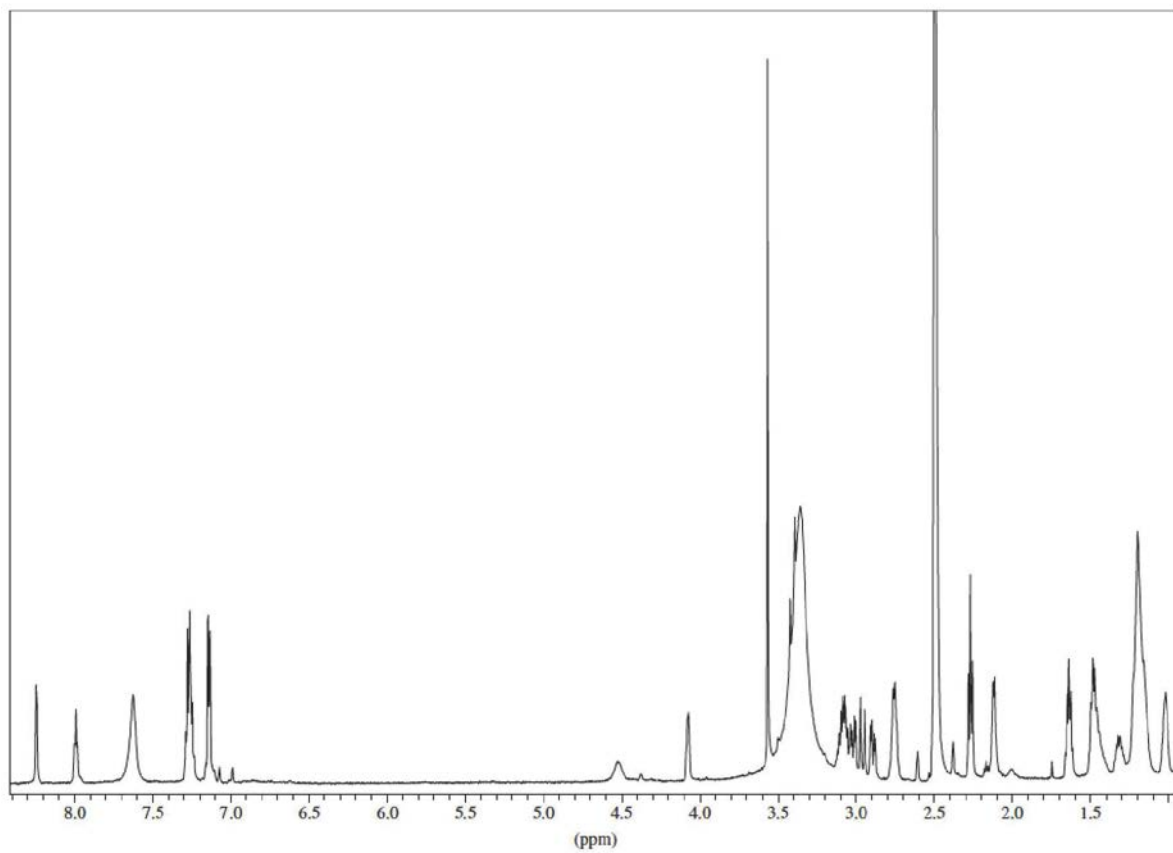


Figure S9. ¹H NMR spectrum of rodriguesic acid methyl ester (5) in DMSO-*d*₆ at 600 MHz.

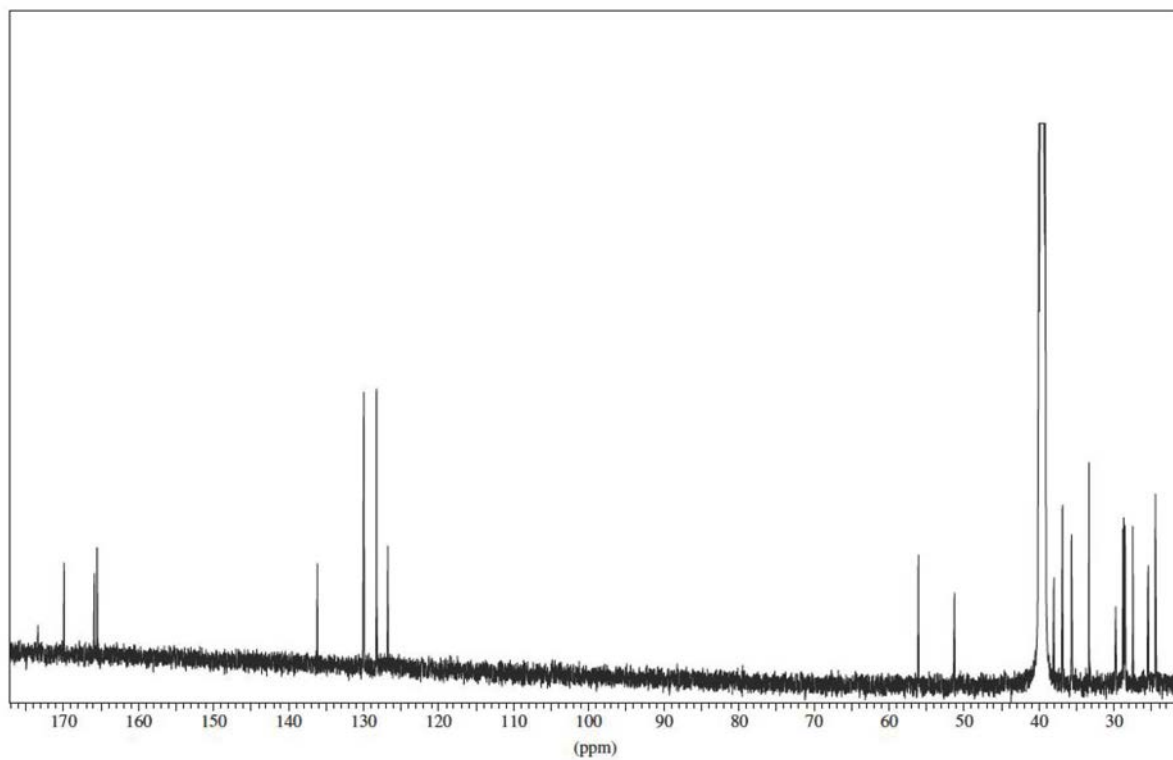


Figure S10. ¹³C NMR spectrum of the rodriguesic acid methyl ester (5) in DMSO-*d*₆ at 150 MHz.

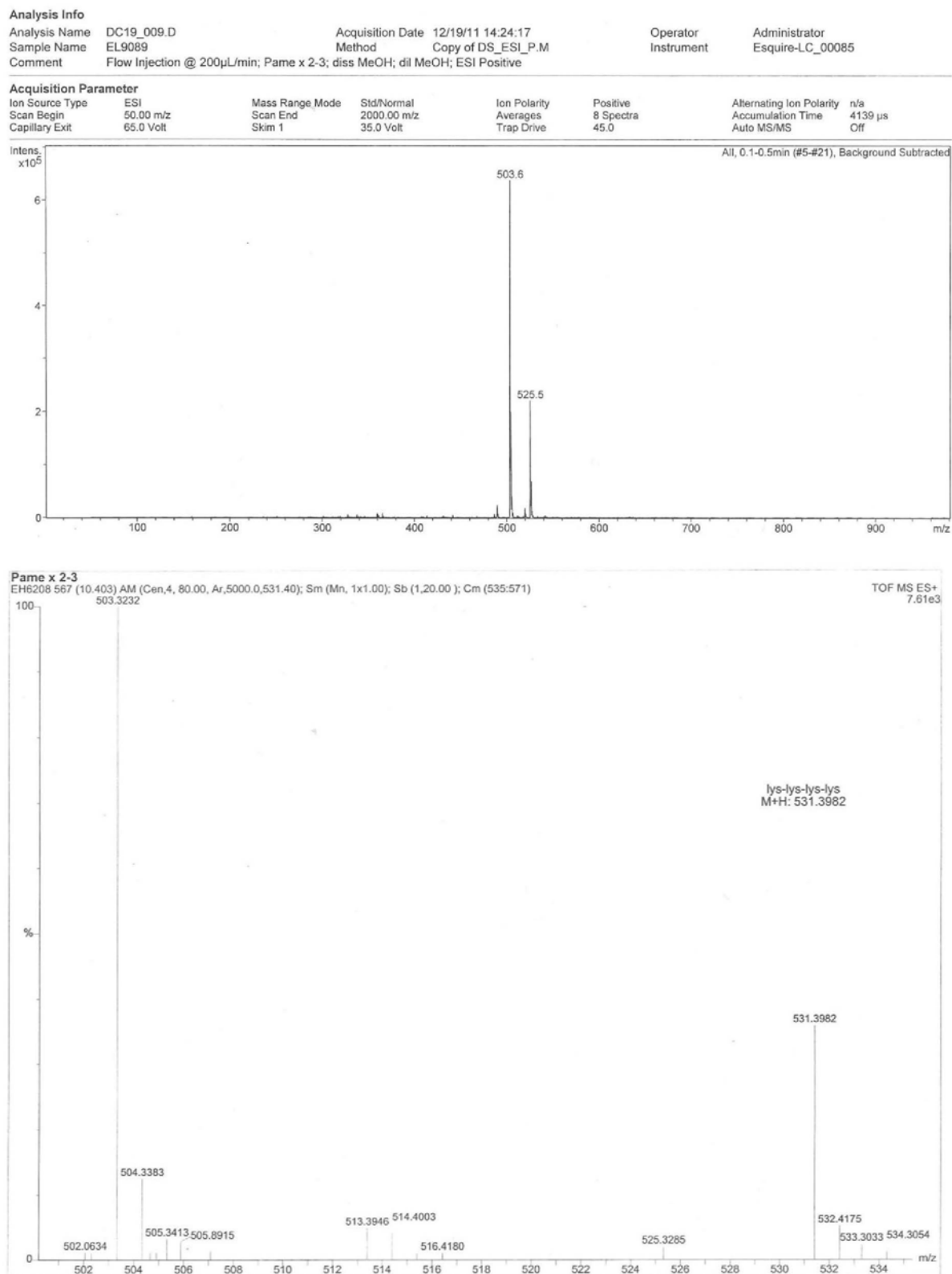


Figure S11. LR-ESI (top) and HR-ESI (bottom) mass spectra of the rodriguesic acid methyl ester (**5**).

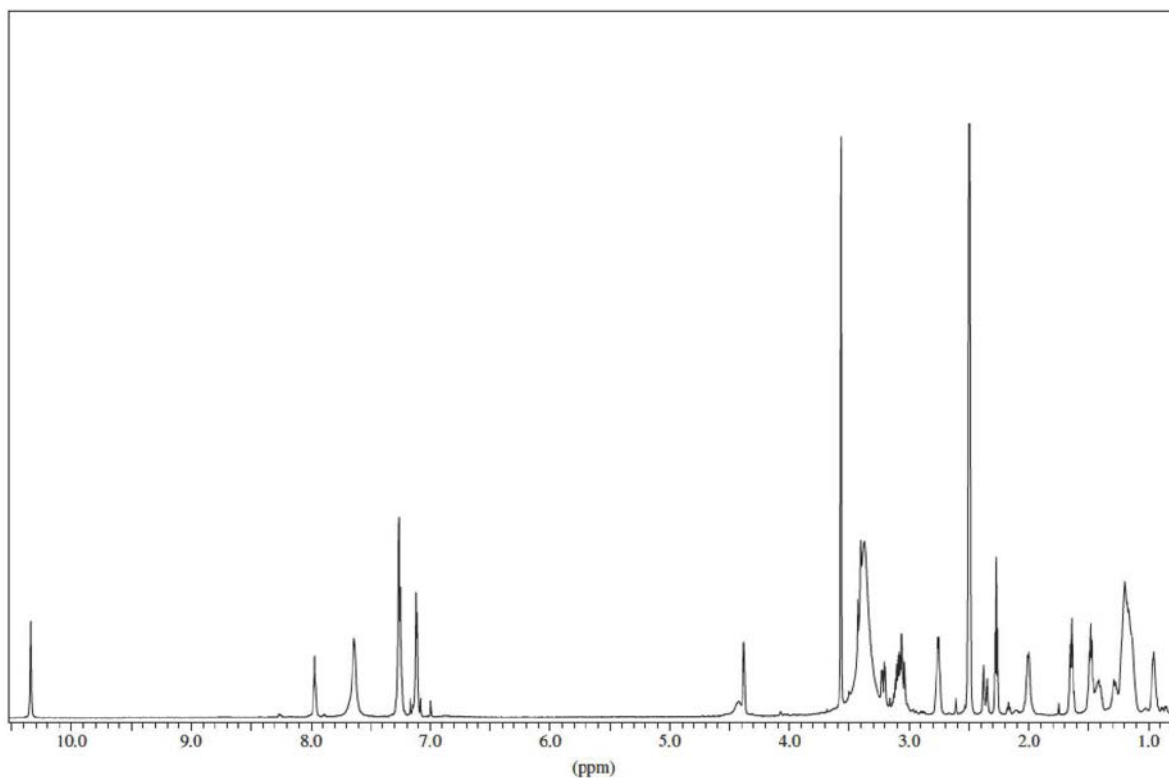


Figure S12. ¹H NMR spectrum of the methyl ester of the rodriguesic acid hydroxamate (**6**) in DMSO-*d*₆ at 600 MHz.

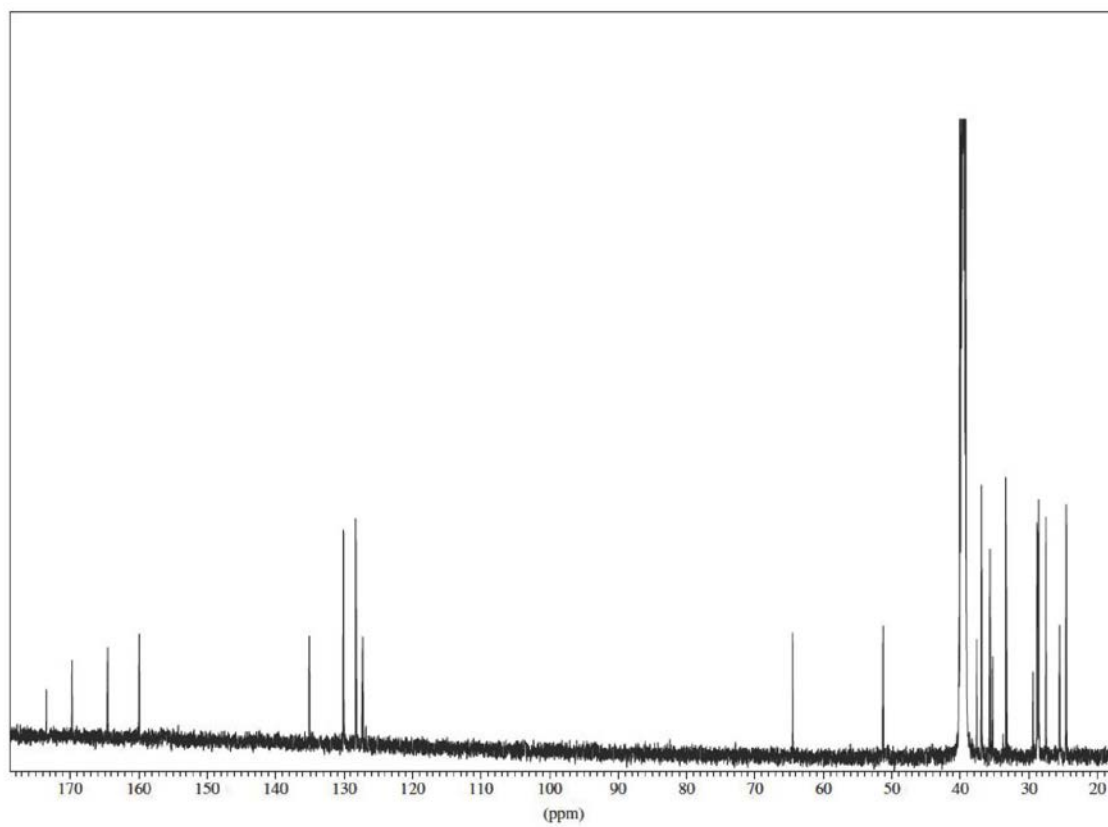


Figure S13. ¹³C NMR spectrum of methyl ester of the rodriguesic acid hydroxamate (**6**) in DMSO-*d*₆ at 150 MHz.

Analysis Info

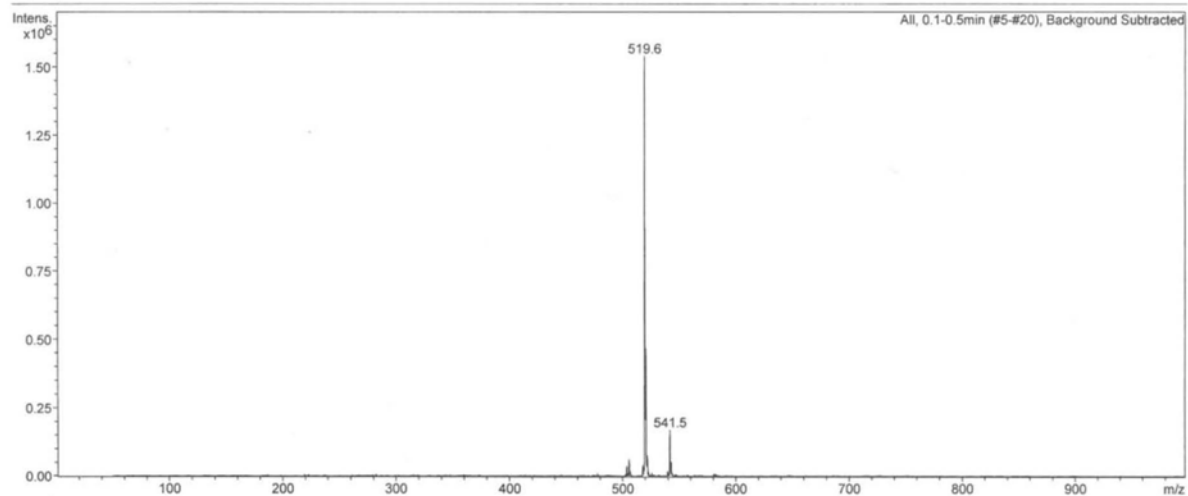
Analysis Name DC19_013.D
Sample Name EL9090
Comment Flow Injection @ 200 μ L/min; Pame x 2-4; diss MeOH; dil MeOH; ESI Positive

Acquisition Date 12/19/11 14:45:22
Method Copy of DS_ESI_P.M

Operator Administrator
Instrument Esquire-LC_00085

Acquisition Parameter

Ion Source Type	ESI	Mass Range Mode	Std/Normal	Ion Polarity	Positive	Alternating Ion Polarity	n/a
Scan Begin	50.00 m/z	Scan End	2000.00 m/z	Averages	8 Spectra	Accumulation Time	4363 μ s
Capillary Exit	65.0 Volt	Skim 1	35.0 Volt	Trap Drive	45.0	Auto MS/MS	Off



Pame x 2-4

EH6209 69 (1.265) AM (Cen,4, 80.00, Ar,5000.0,531.40); Sm (Mn, 1x1.00); Sb (1,20.00); Cm (54:73)

TOF MS ES+
1.02e4

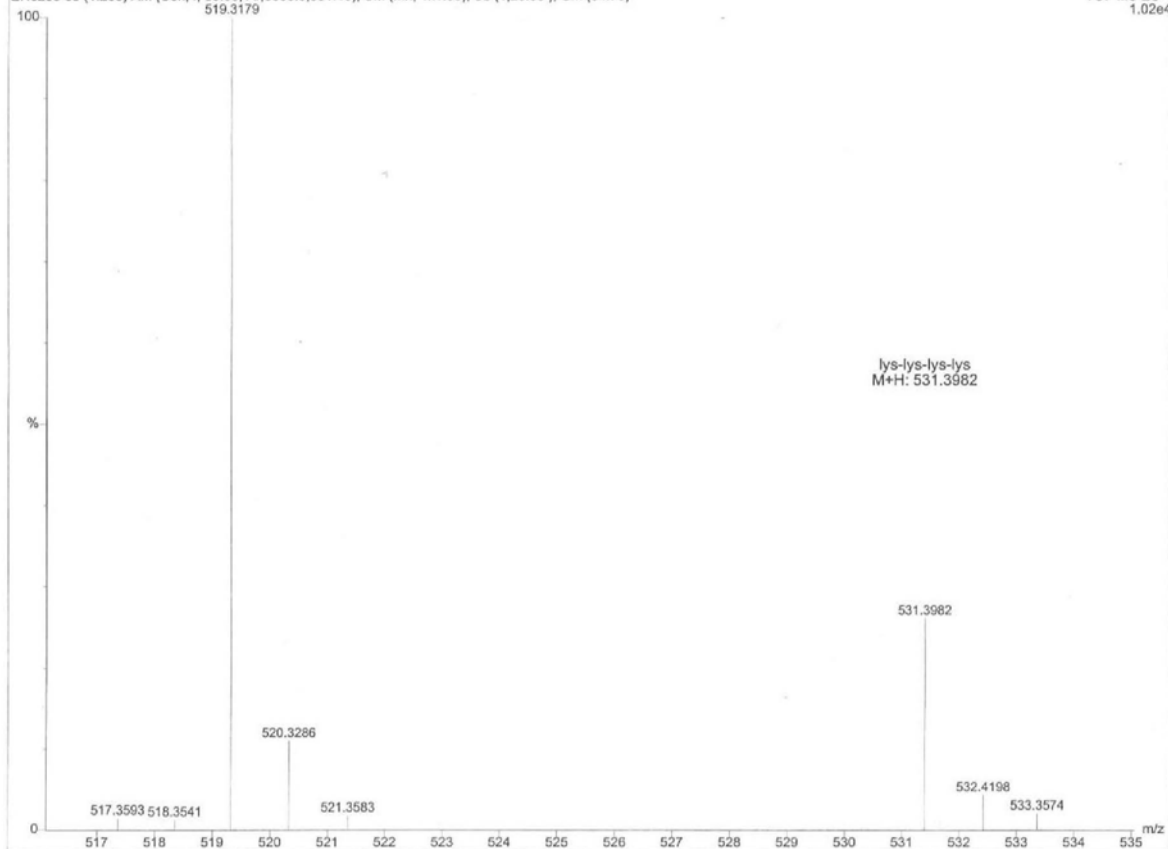


Figure S14. LR-ESI (top) and HR-ESI (bottom) mass spectra of methyl ester of the rodriguesic acid hydroxamate (6).

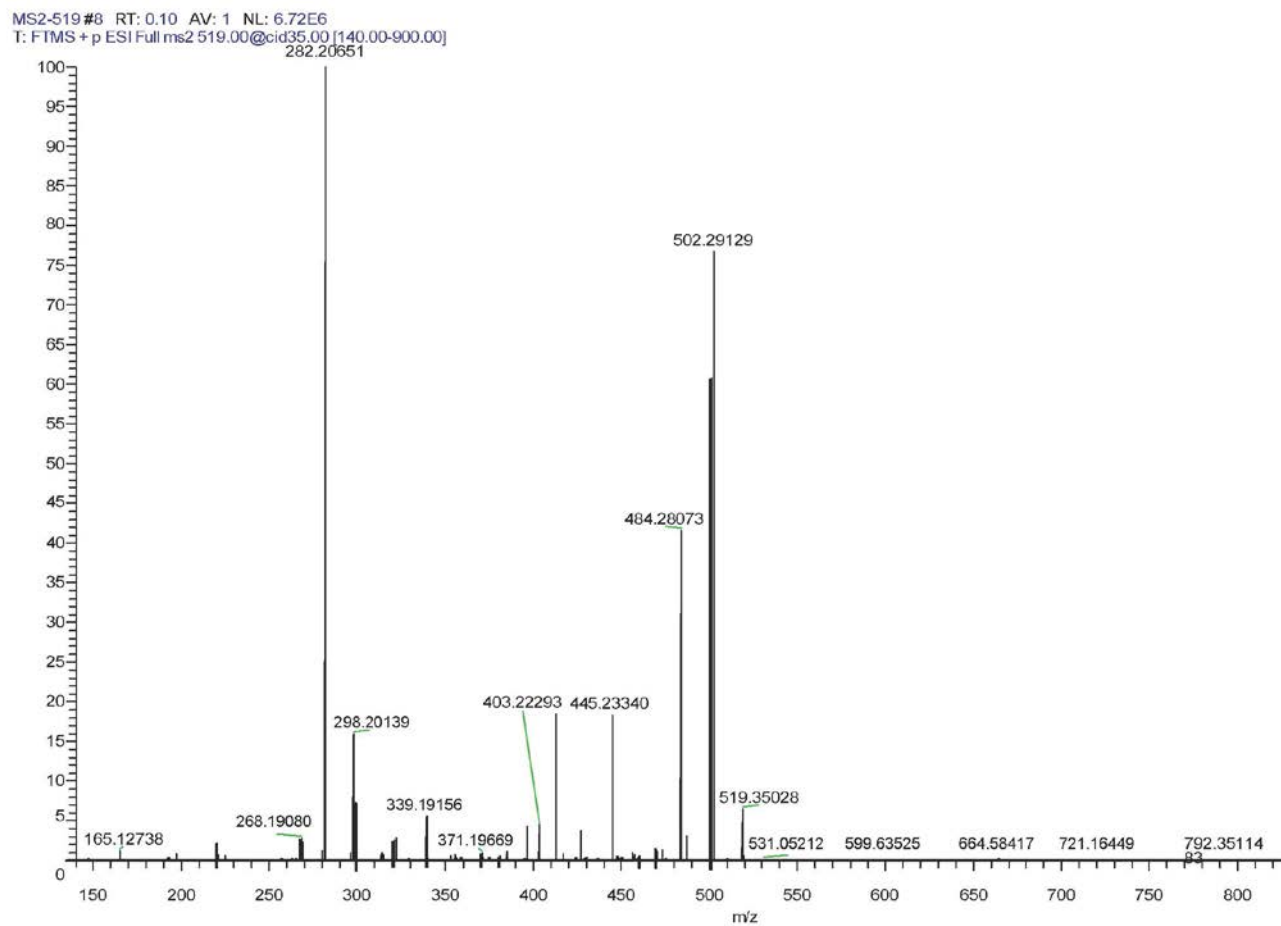


Figure S15. HRFTMS/MS analysis of methyl ester of the rodriguesic acid hydroxamate (**6**) [M+H]⁺ ion at m/z 519.31476.

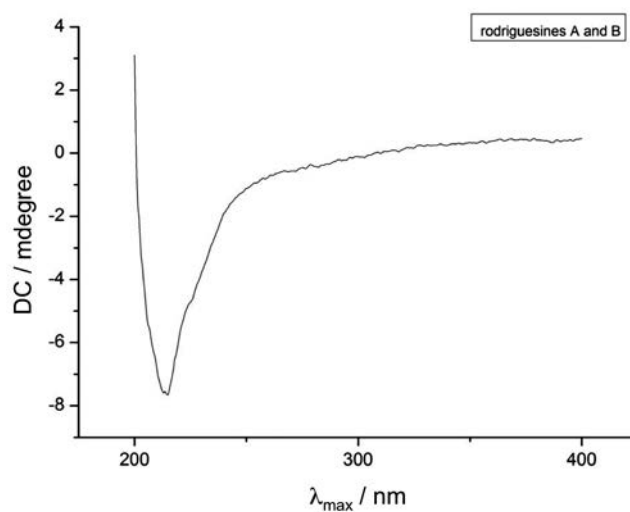


Figure S16. Circular dichroism spectrum of rodriguesines A (**1**) and B (**2**) in MeOH (0.030 mg mL⁻¹).

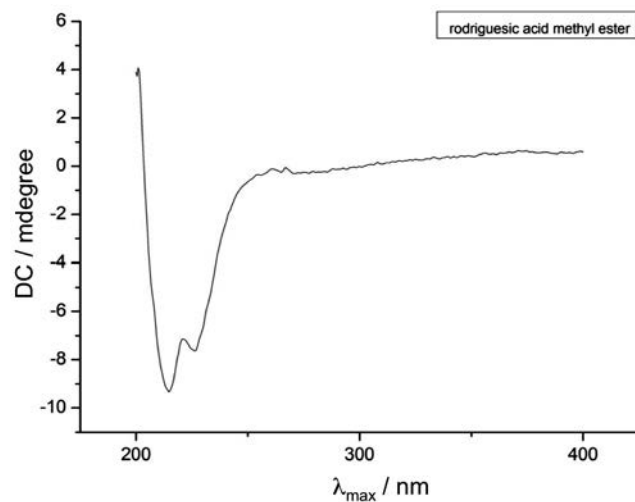


Figure S17. Circular dichroism spectrum of rodriguesic acid methyl ester (5) in MeOH (0.033 mg mL⁻¹).

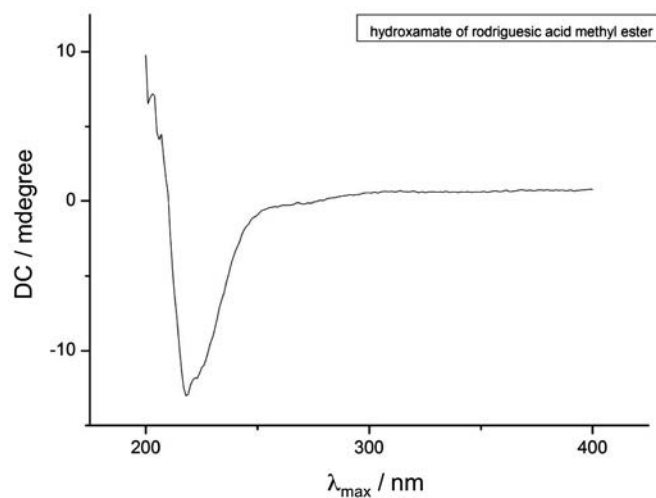


Figure S18. Circular dichroism spectrum of the hydroxamate of rodriguesic acid methyl ester (6) in MeOH (0.2 mg mL⁻¹).