

Centrifugal partition chromatography: efficient tool to access highly polar and unstable synthetic compounds in large scale

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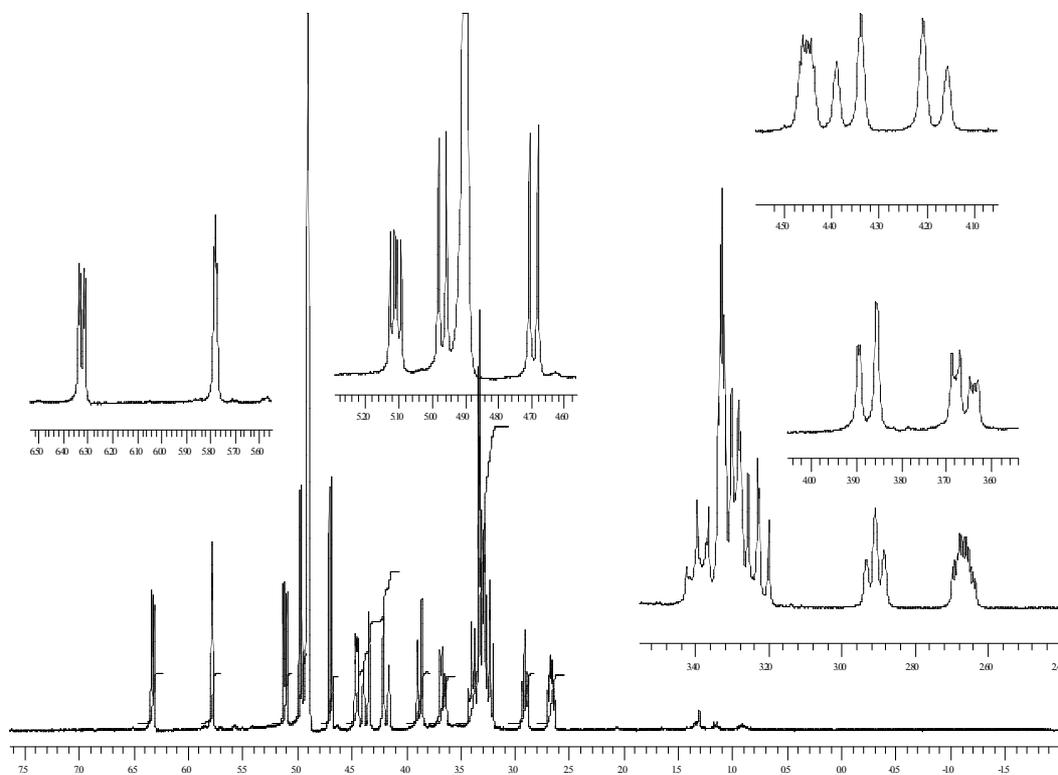
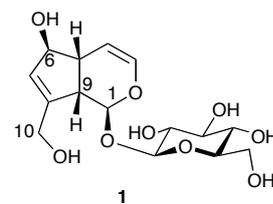
General information. Optical rotations were measured (*c*: g/L) with a *Perkin-Elmer 341* polarimeter. NMR spectra were recorded on *Bruker Avance-400* and/or *Bruker Avance-300* spectrometers, chemical shifts are expressed in ppm downfield to TMS. When necessary, all structures of the novel compounds were insured and the signals unambiguously assigned by 2D NMR techniques: ^1H - ^1H COSY, ^1H - ^1H NOESY, ^1H - ^{13}C HMQC, and ^1H - ^{13}C HMBC. These experiments were performed using standard Bruker microprograms. Chemical shifts are reported in ppm and corrected to δ_{H} 4.79 for D_2O , δ_{H} 3.34 for CD_3OD . Chemical shifts are reported in ppm and corrected to δ_{C} 49.86 for CD_3OD as internal reference. Splitting patterns in the ^1H NMR spectra are designated as s, singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; m, multiplet; br, broad. ESI-MS were determined on *ZQ2000 Waters* or *LCT KE383* and HR-ESI-MS on a *Waters Micromass Q-TOF* apparatus equipped with a ESI-Z spray source. Elemental analyses were obtained by Service for Elemental Analysis at ICSN-CNRS, 91198 Gif-sur-Yvette, Cedex (France). TLC were performed on *Merck Silica gel 60 F254* aluminium sheets, using vanillin/ H_2SO_4 as spray reagent. Yields refer to chromatographically and spectroscopically pure compounds. Trivial nomenclature of iridoids was employed.

CPC was performed on SCPC-250+1000-B apparatus provided by Armen Instrument (Saint-Avé, France) fitted with two rotors (total volume: 250 mL or 1 L), containing respectively 1953 or 2016 twin-cells. Rotation speed was adjusted to 1600 rpm for the 250 mL rotor and to 1000 rpm for the 1 L rotor. A valve incorporated in the CPC apparatus allowed operation in ascending or descending mode. The system is equipped with a gradient pump and a 10 mL or a 50 mL loop injection 6-way valve. Fractions were collected by a Büchi 684 fraction collector (Flawil, Switzerland). The chromatographies were conducted at room temperature. Obtained fractions were analyzed by TLC observation under UV light and revelation with sulfuric vanillin and heating.

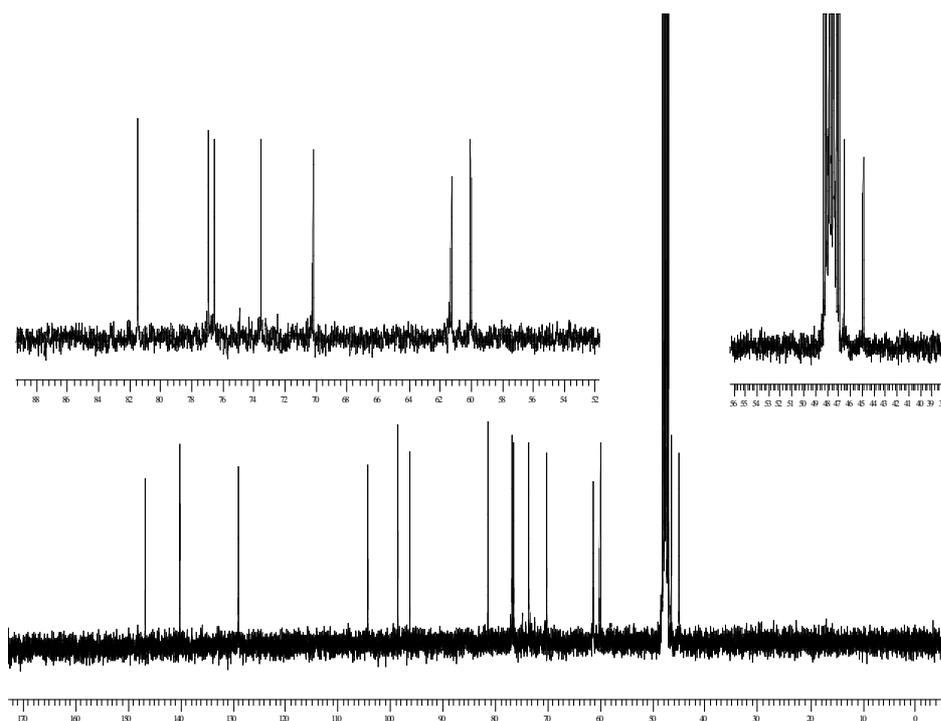
HPLC analysis was performed on LaChrom Elite apparatus provided by VWR (Fontenay-sous-Bois, France) with a D-7000 interface, a L-7200 autosampler, a L-7100 pump, a L-7400 UV detector, and running on EZChrom Elite 3.3 software. ODS reverse phase column (phenomenex, 150 mm \varnothing 4.6 mm, 5 μm) was used for analysis.

Aucubin (1)

^1H NMR of aucubin (1):

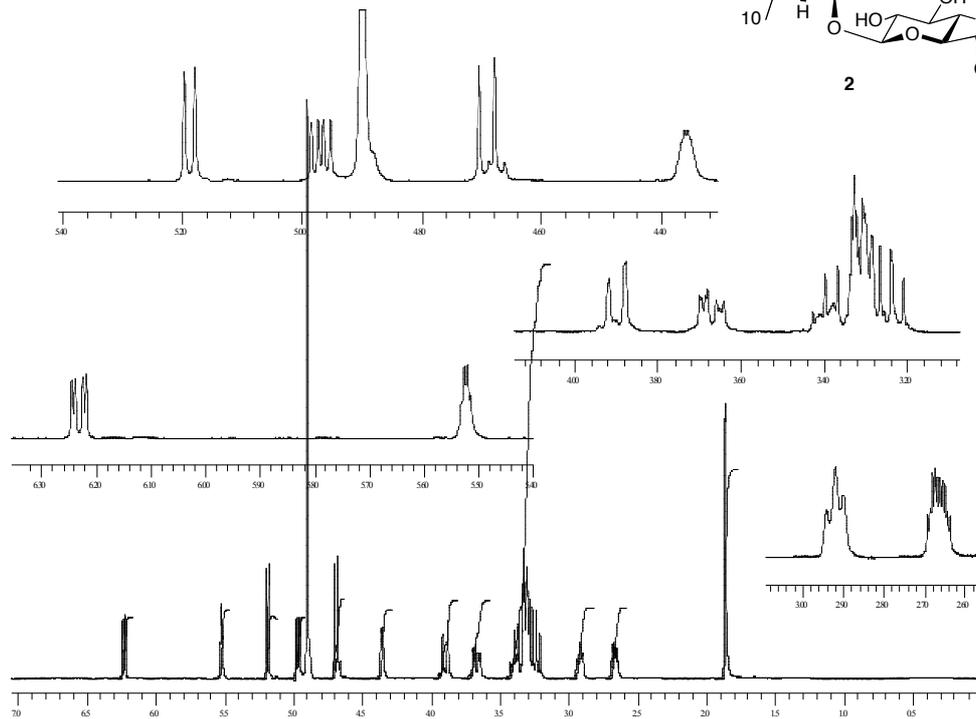
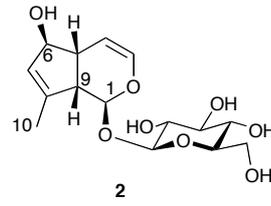


^{13}C NMR of aucubin (1):

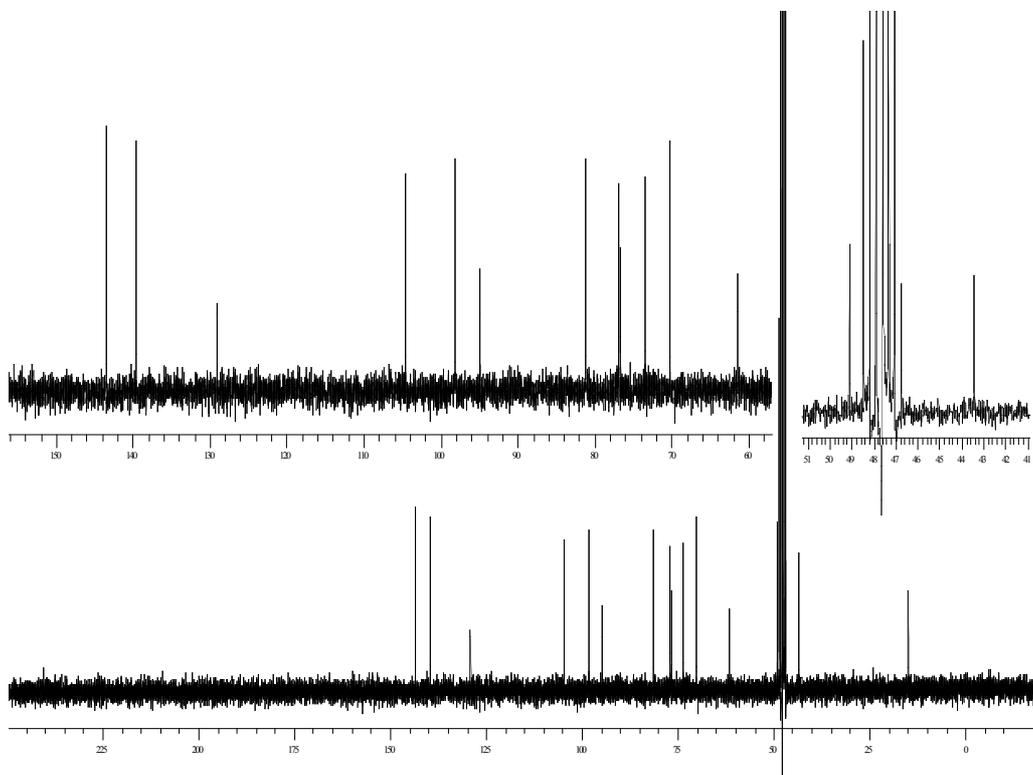


Linaride (2) (10-Monodeoxyaucubin)¹

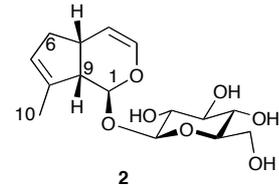
¹H NMR of linaride (2):



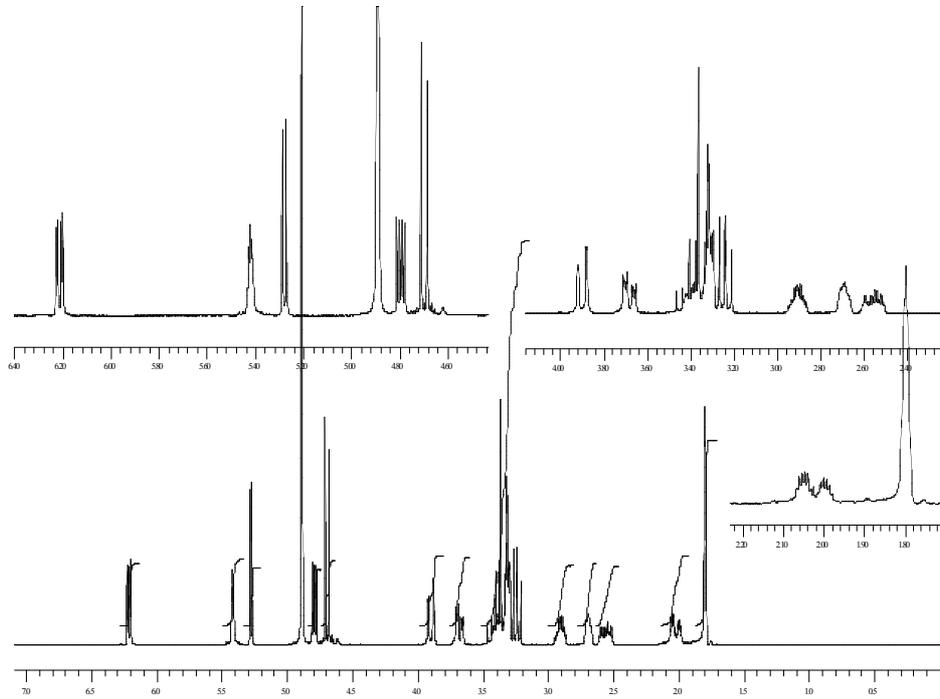
¹³C NMR of linaride (2):



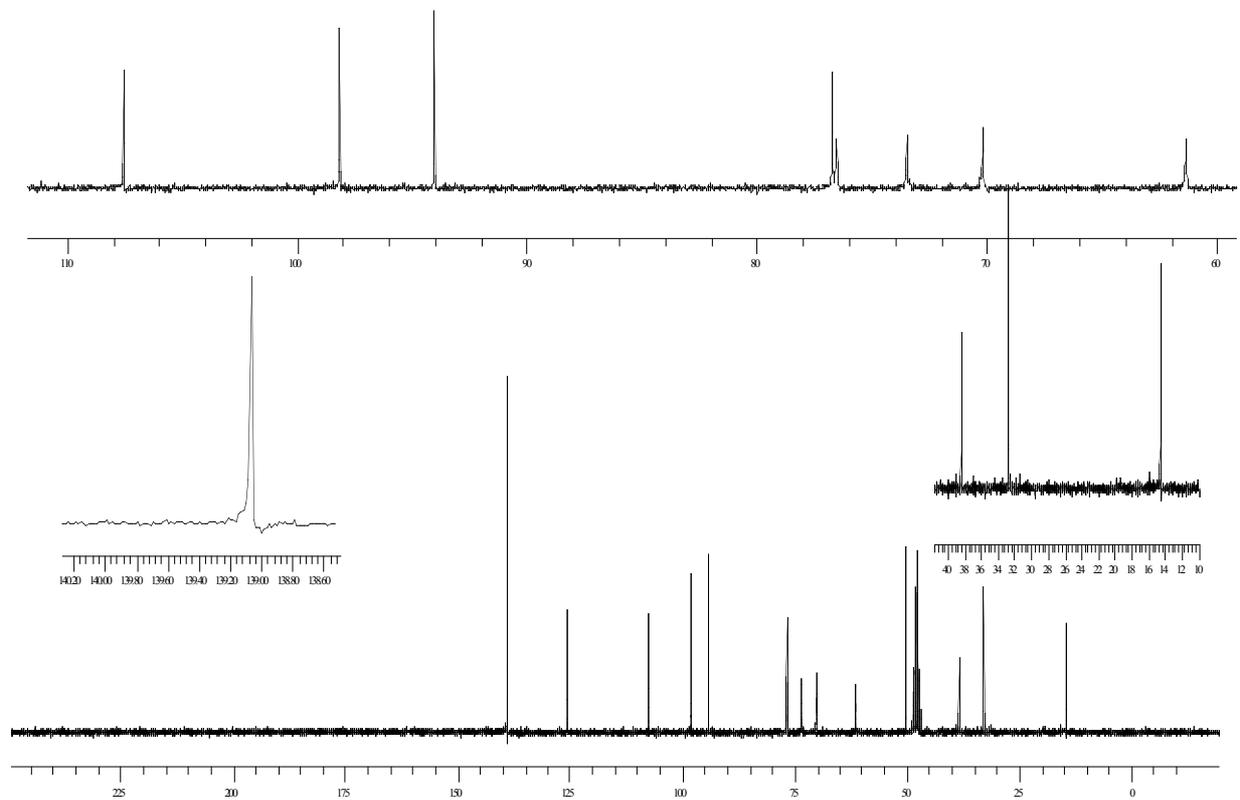
6',10-Dideoxyaucubin (3)²



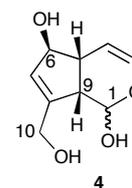
¹H NMR of 6,10-Dideoxyaucubin (3):



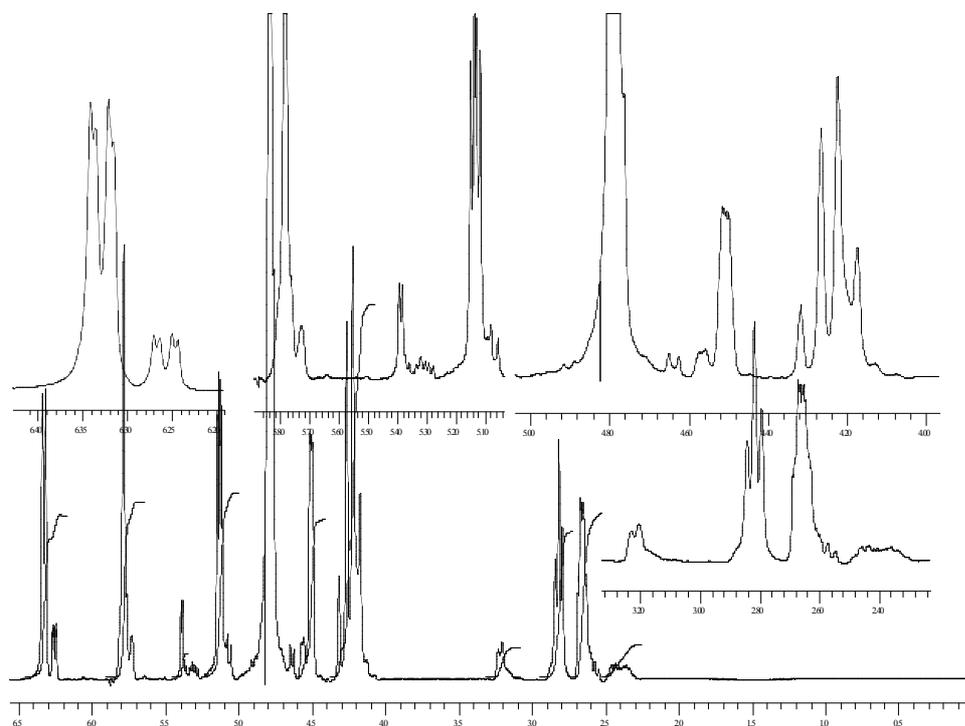
¹³C NMR of 6,10-Dideoxyaucubin (3):



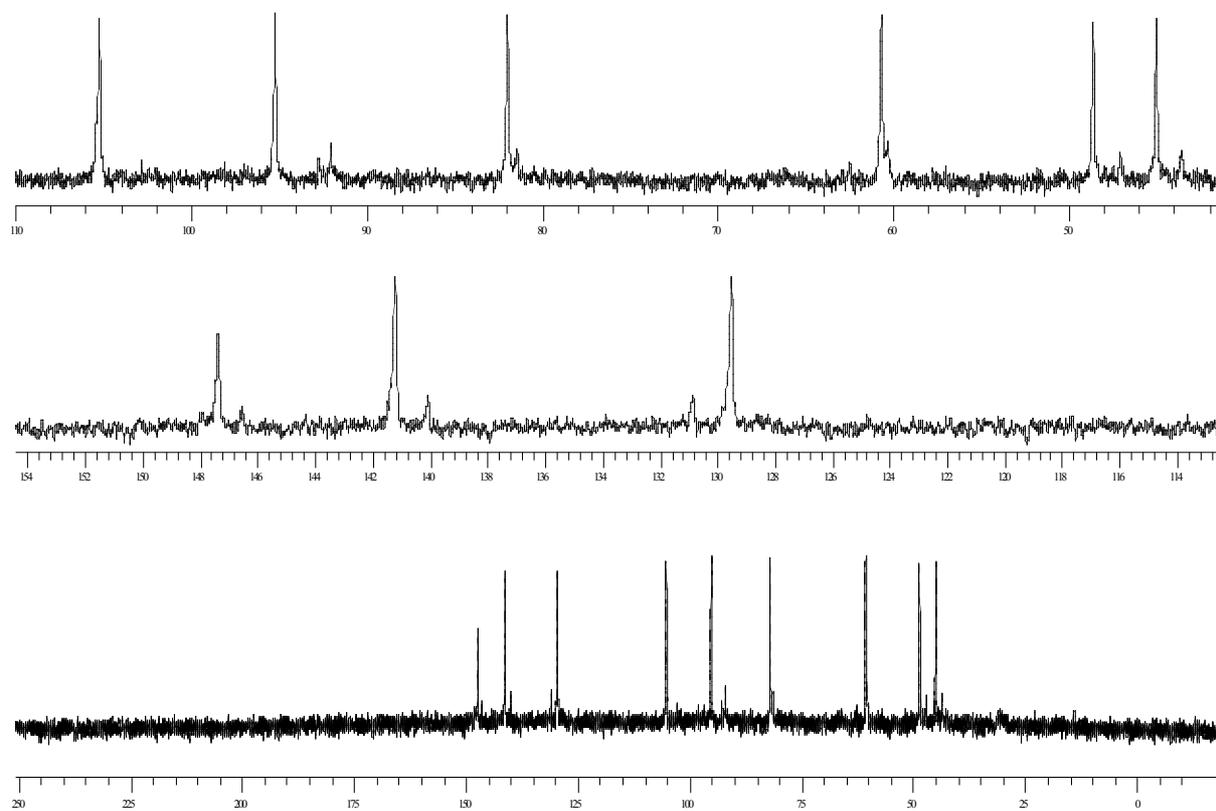
Aucubigenin (4)³



¹H NMR of aucubigenin (4).

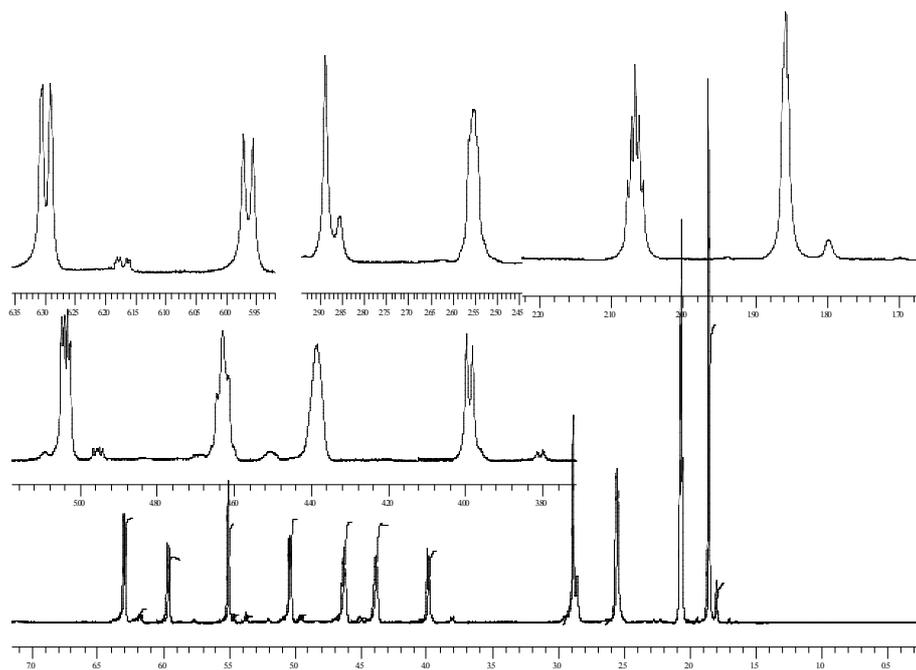
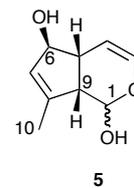


¹³C NMR of aucubigenin (4).

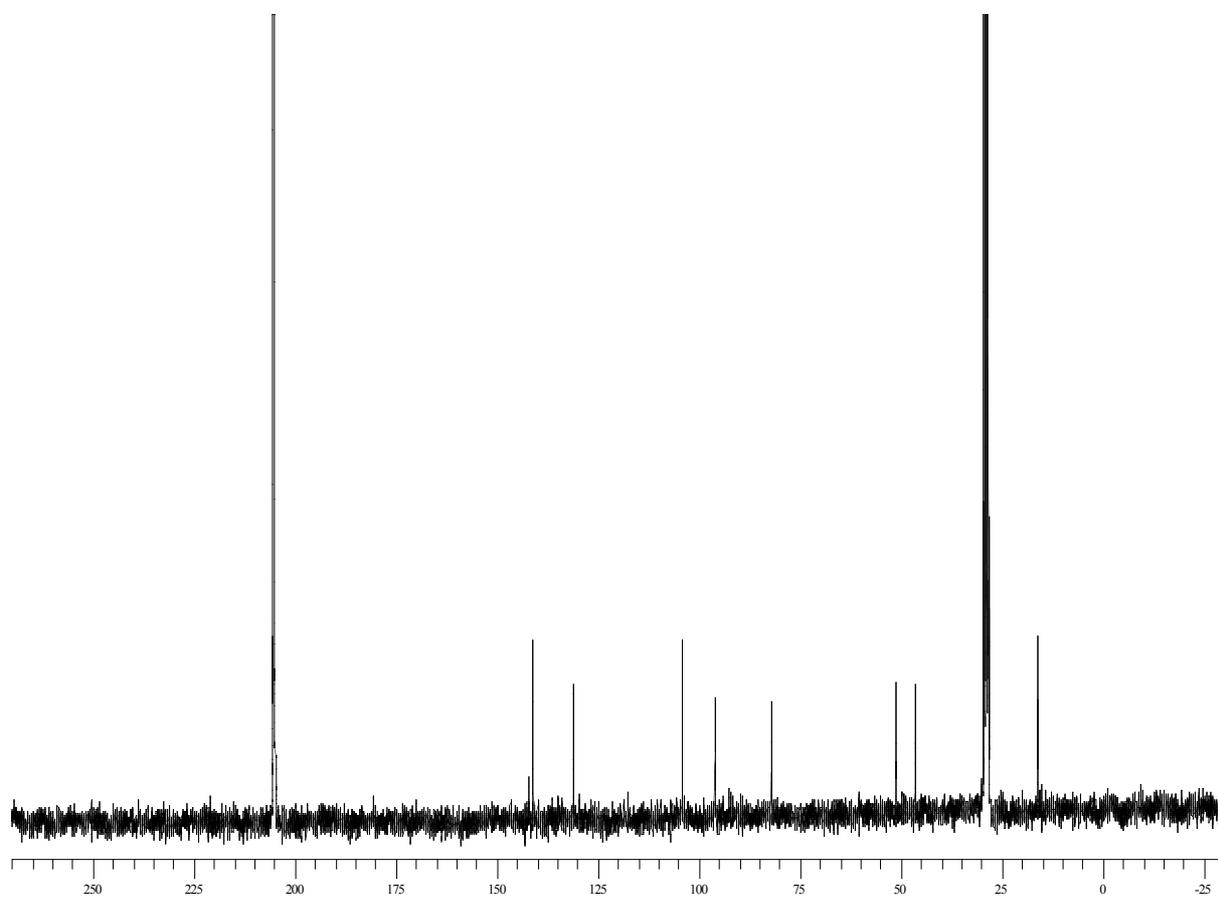


10-Monodeoxyaucubigenin (5)⁴

¹H NMR of 10-monodeoxyaucubigenin (5)

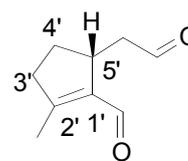


¹³C NMR of 6'-monodeoxyaucubigenin (5):

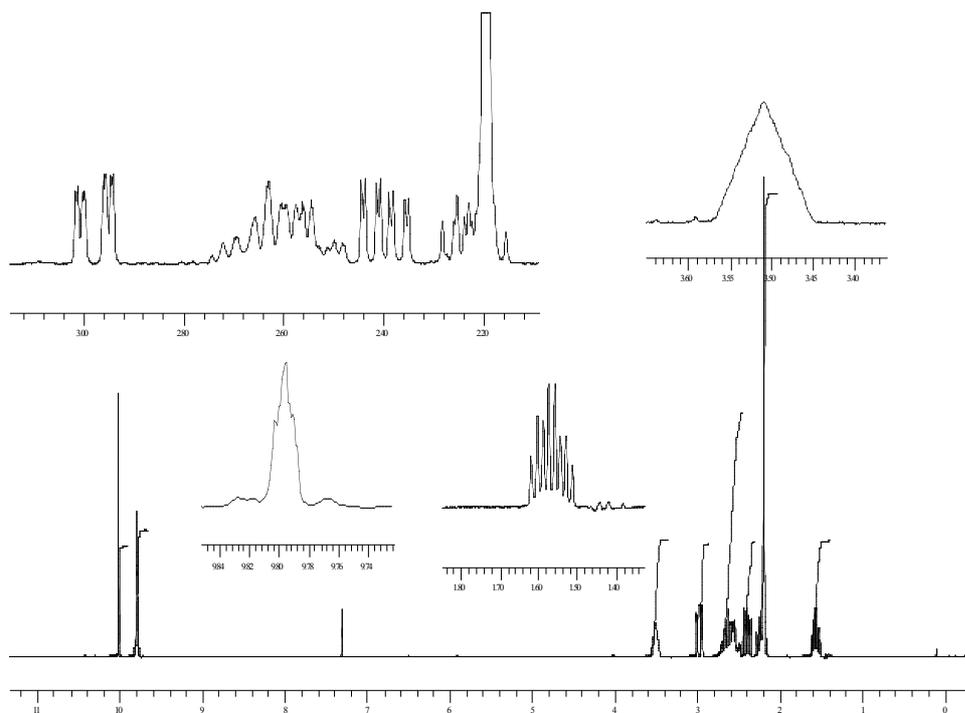


(*R*)-Rotundial [(*R*)-2'-methyl-5'-(2''-oxoethyl)cyclopent-1'-enecarbaldehyde] (6)

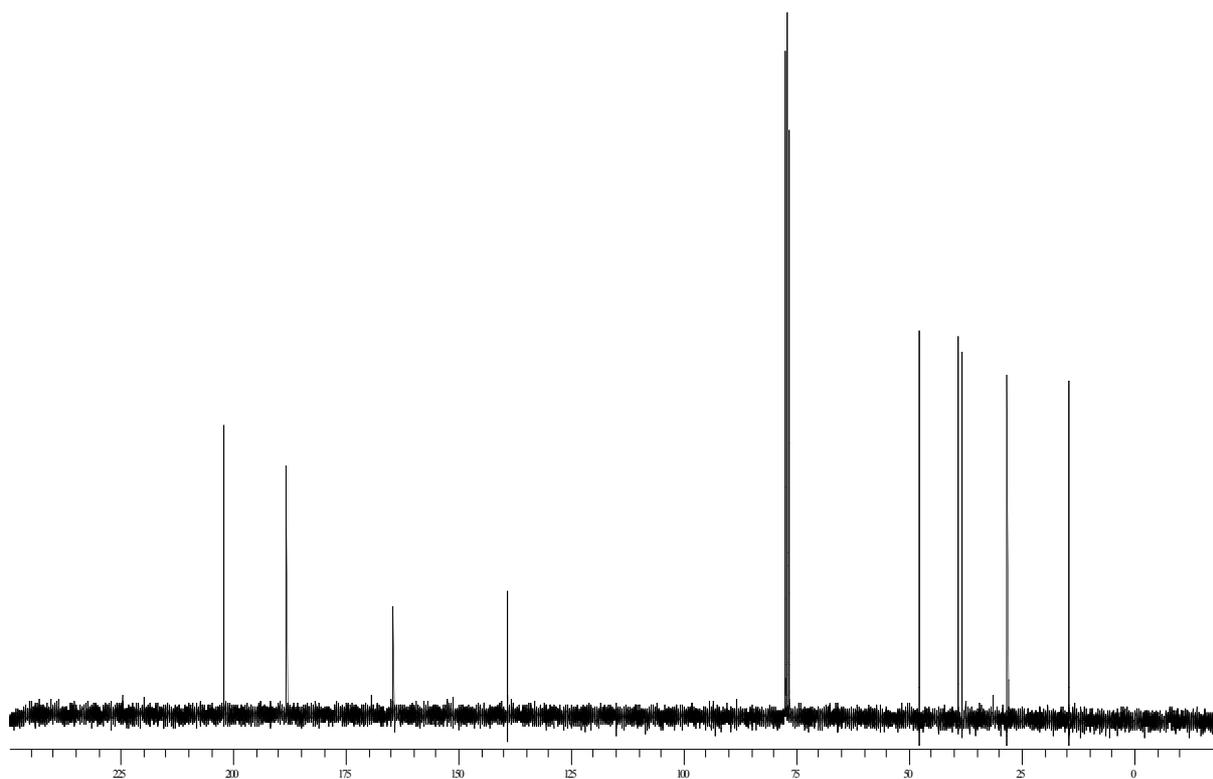
The data of **6** were identical to those described in the literature.^{5,6}



¹H NMR of (*R*)-Rotundial (**6**):



¹³C NMR of (*R*)-Rotundial (**6**):



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- ¹ E. Davini, C. Iavarone, F. Mataloni and C. Trogolo, *J. Org. Chem.*, 1988, **53**, 2089.
- ² A. Bianco, P. Passacantilli, G. Polidori, M. Nicoletti and I. Messina, *Gazzetta Chim. Ital.*, **1983**, 113, 829.
- ³ E. Davini, C. Iavarone, C. Trogolo, P. Aureli and B. Pasolini, *Phytochemistry*, 1986, **25**, 2420
- ⁴ A. Bianco, M. Guiso, C. Iavarone, P. Passacantilli and C. Trogolo, *Tetrahedron*, 1977, **33**, 851
- ⁵ H. Takikawa, Y. Yamazaki and K. Mori, *Eur. J. Org. Chem.* 1998, 229.
- ⁶ E. Marqués-López, R. P. Herrera, T. Marks, W. C. Jacobs, D. Könnig, R. M. de Figueiredo and M. Christmann, *Org. Lett.* 2009, **11**, 4116.