S1 Supporting Information

Tyrosyl-DNA Phosphodiesterase I Inhibitors from an Australian Plant *Macropteranthes leichhardtii*

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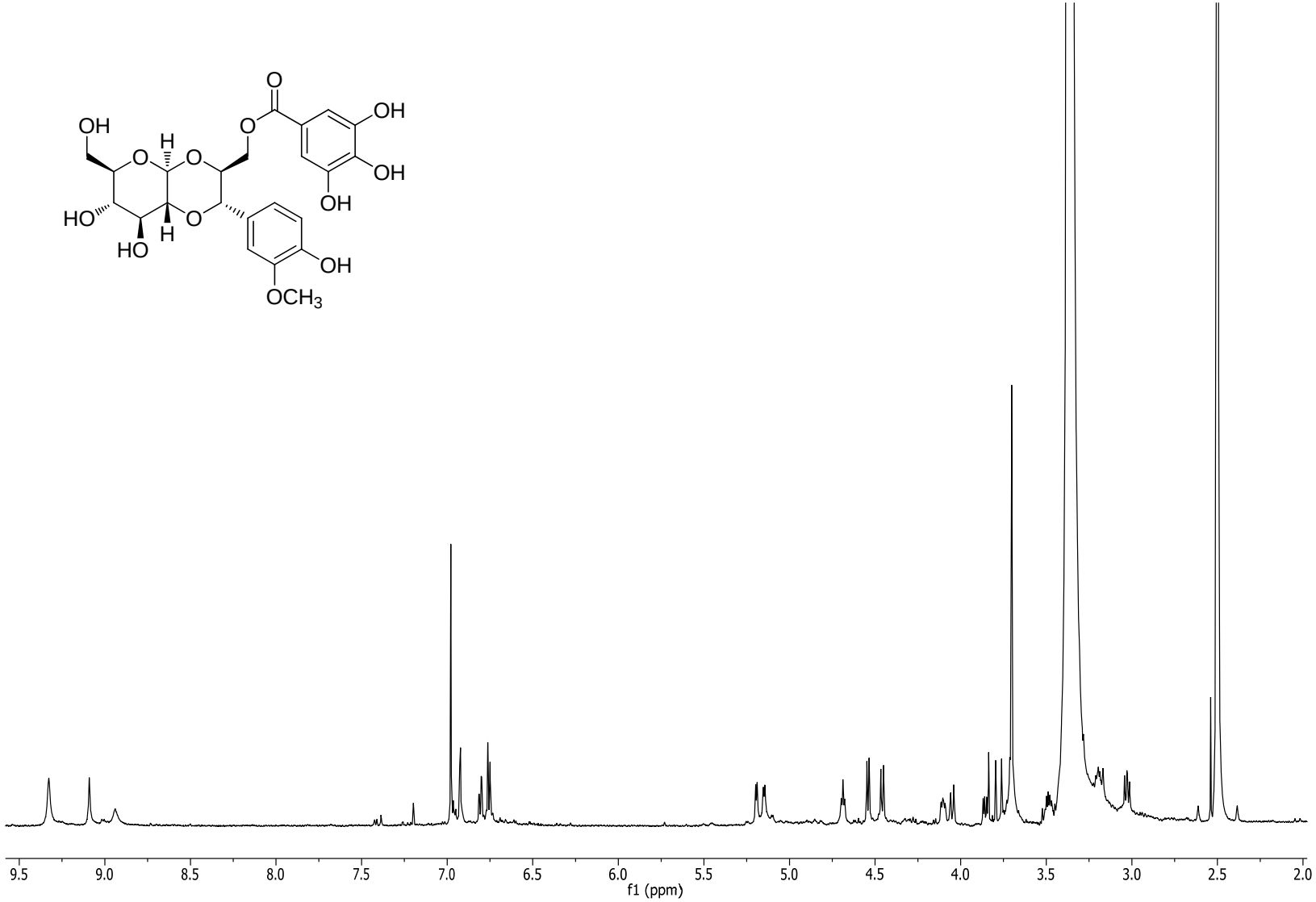
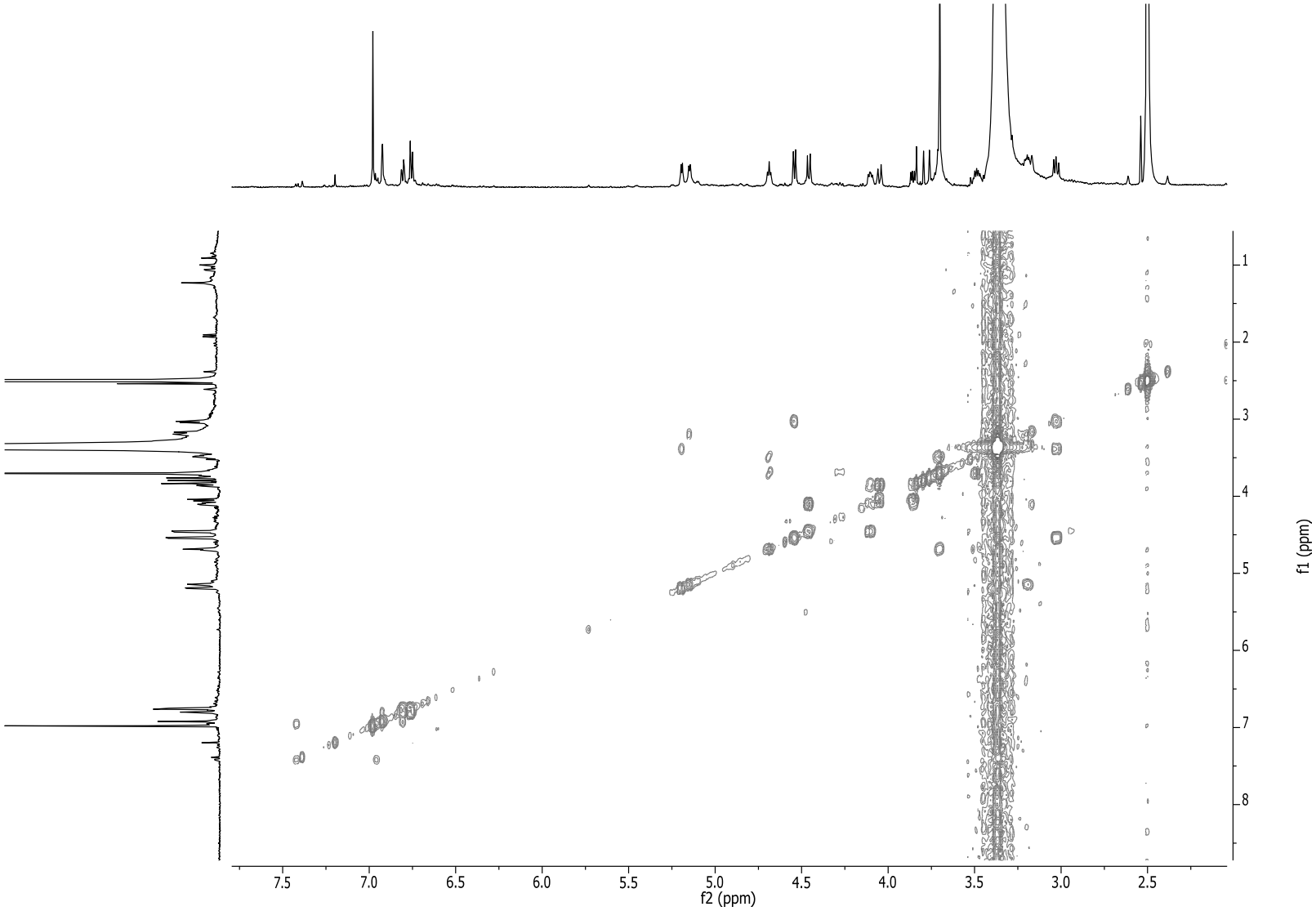
Contents:

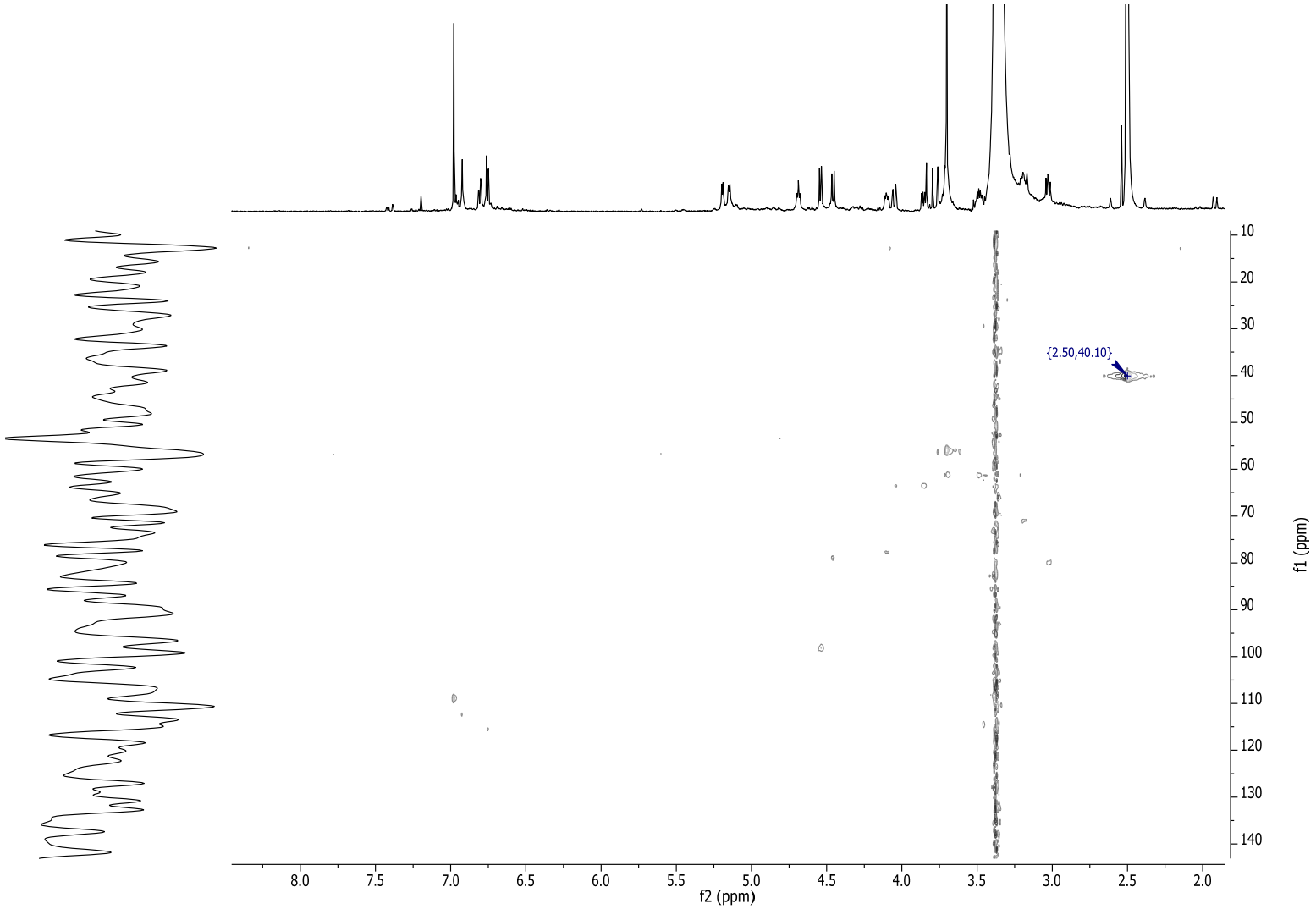
S2 ^{1}H NMR spectrum for macropteranthol (**1**) in DMSO-d_6



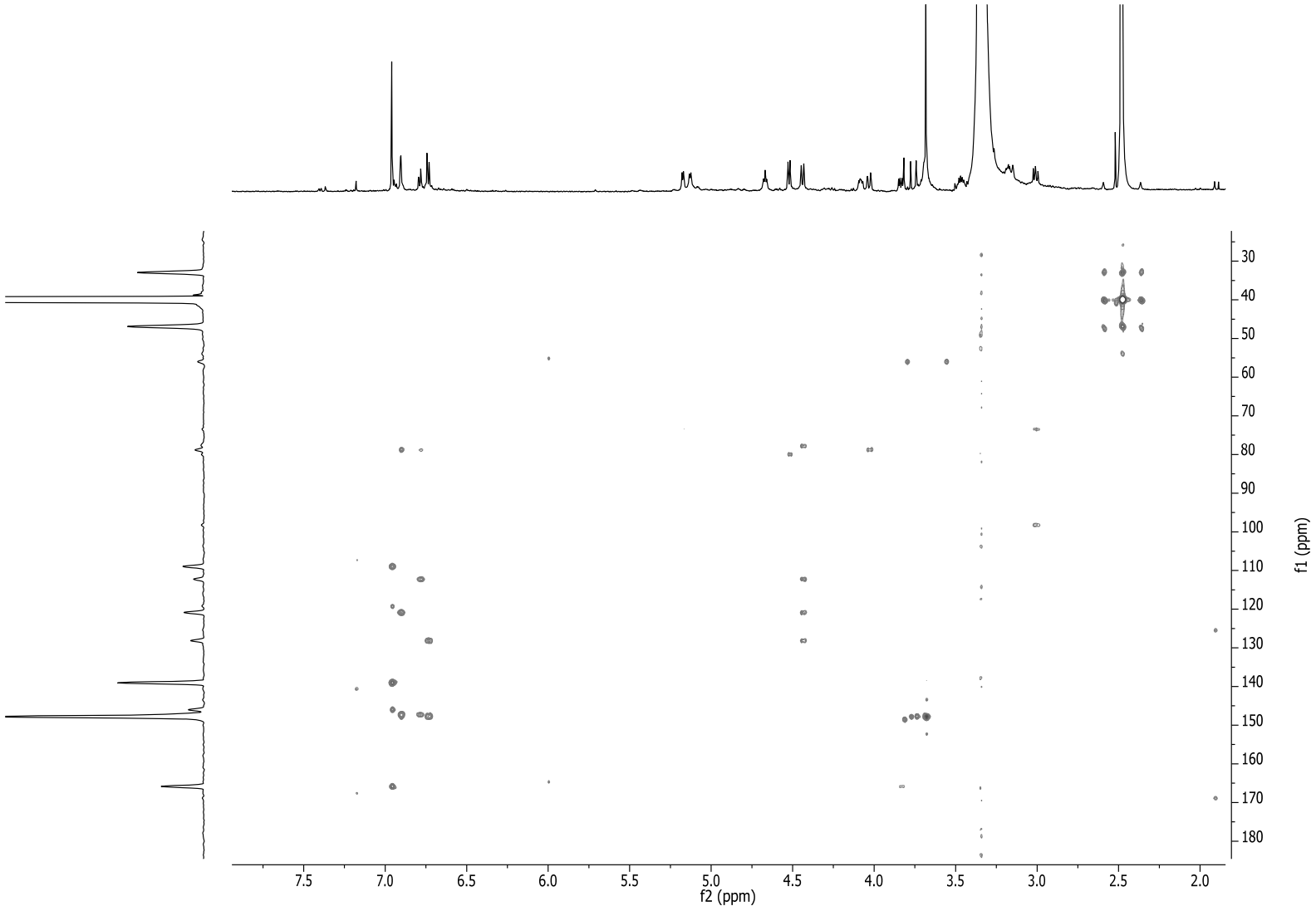
S3 gCOSY spectrum for macropteranthol (**1**) in DMSO-d_6



S4 gHSQC spectrum for macropteranthol (**1**) in DMSO-d_6



S5 gHMBC spectrum for macropteranthol (**1**) in DMSO-d_6



S6 Calculated Boltzmann distributions and optical rotations for each conformer of **1**

Conformer	HF		DFT	
	Boltzmann distribution (%)	Optical rotation	Boltzmann distribution (%)	Optical rotation
1	16.23	27.38	2.70	13.6
2	16.23	27.38	2.70	13.68
3	0.36	49.71	0.16	61.11
4	0.76	-6.82	79.93	0.03
5	4.55	36.88	1.49	98.34
6	0.66	7.81	0.25	-39.2
7	13.84	26.11	2.46	107.21
8	24.61	-7.92	3.49	-29.85
9	1.68	25.53	0.93	262.96
10	2.27	79.34	0.96	202.4
11	2.11	88.87	0.91	219.66
12	10.14	16.23	1.87	17.07
13	5.59	49.93	1.23	101.82
14	0.99	123.19	0.93	262.68
Weighted optical rotation		22.17		14.21

S7 Acid hydrolysis of compound (5)

In a typical hydrolysis, compound **5** (0.3 mg) was heated in 2 N HCl (1 mL) at 70 °C for 4 h. The resulting hydrolysate was analyzed by LC-MS. The LC-MS result revealed that compound **5** was not detected and the aglycone {+ESIMS *m/z* 199 $[M + H]^+$} and sugar part {+ESIMS *m/z* 333 $[M + H]^+$} were appeared. The hydrolysate was dried under vacuum and then was pre-adsorbed to cotton, following by packing into a stainless steel cartridge (10 × 30 mm) that was subsequently attached to a C_{18} preparative HPLC column. Isocratic HPLC conditions of 90% H_2O (0.1% TFA)/10% MeOH (0.1% TFA) were initially employed for the first 10 min, then a linear gradient to 100% MeOH (0.1% TFA) was run over 40 min, followed by isocratic conditions of 100% MeOH (0.1% TFA) for a further 10 min, all at a flow rate of 9.0 mL/min. Fraction 5 contained the aglycone (0.1 mg) which gave an $[\alpha]_D$ -6.2, (*c* 0.005, MeOH), while standard 8(*S*)-1,2-diol-3-(4-hydroxy-3-methoxy-phenyl) propane hand an $[\alpha]_D$ -23, (*c* 0.69, EtOH) and 8(*R*)-isomer an $[\alpha]_D$ +18, (*c* 0.73, EtOH).