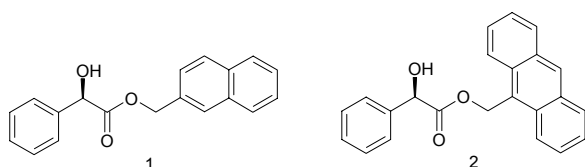


Absolute structure and optical rotation of new *R*-mandelic acid esters, Jacek Grochowski,^{a,*} Michał Markiewicz,^b Paweł Serda,^a Barbara Rys^{ca} and Anna Stankiewicz^c, ^a*Regional Laboratory of Physicochemical Analysis and Structural Research*, ^b*Faculty of Chemistry and* ^c*Department of Organic Chemistry*; Jagiellonian University, Ingardena 3, 30-060 Krakow, Poland. E-mail: grochows@chemia.uj.edu.pl

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The new *R* mandelic acid esters (*R*)-(-)-2-naphthylmethyl-hydroxy(phenyl)acetate (**1**) and (*R*)-(-)-9-anthrylmethyl-hydroxy(phenyl)acetate (**2**) were obtained by esterification of optically-controlled (*R*)-(-)-mandelic acid with respectively 9-anthryldiazomethane and 2-naphthylidiazomethane in dry ether at room temperature.



The products were purified by column chromatography followed by crystallization from CCl₄. The OR calculations, which were based on the molecular structures determined by X-ray diffraction, were undertaken using the DFT method with GIAOs for various wavelengths within the range 500 to 590 nm in vacuum and selected solvents. The polarized continuum model (PCM) was used to incorporate the influence of the solvent[1]. Compound **1**, orthorhombic, space group $P2_12_12_1$, $a = 5.7830(1)$, $b = 7.9965(1)$, $c = 32.3937(5)$ Å, $V = 1498.01(4)$ Å³, $Z = 4$, $D_x = 1.296$ Mg m⁻³. Compound **2**, monoclinic, space group $P2_1$, $a = 8.5570(2)$, $b = 7.6561(1)$, $c = 13.4389(3)$ Å, $\beta = 100.683(1)^\circ$, $V = 865.16(3)$ Å³, $Z = 2$, $D_x = 1.314$ Mg m⁻³. For **1** and **2** X-ray data were collected using a KappaCCD diffractometer and MoK α radiation with a data resolution of 0.77 ($\theta_{\max} \sim 27.5^\circ$, completeness 97.4% and 99.7% respectively), providing similar data-to-parameter ratios of 12.7 and 12.85 respectively. Structure solution was carried out by direct methods and full-matrix least-squares refinement against $|F|^2$ gave good R indices: (**1**) $R = 0.0397$, $wR(|F|^2) = 0.0764$; (**2**) $R = 0.0351$, $wR(|F|^2) = 0.0829$, for $I > 2 \sigma(I)$. Maximum features on the final difference electron-density maps were below 0.2 eÅ⁻³ in both cases. The Flack (1983) parameter x was refined using the TWIN/BASF option in SHELXL97 and converged to 0.2(1.1) and 0.8(9) for **1** and **2** respectively. Thus the absolute structure could not be confirmed from the resonant scattering of the three oxygen atoms per molecule. However, in both cases, the absolute configuration at the chiral centre was set to *R*, in agreement with the synthesis undertaken using enantiopure *R* enantiomers as starting materials.

[1] Canes, M. T. , Mennucci B. & Tomasi, J. (1997). *J. Chem. Phys.* **107**, 3032