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An approach to the synthesis and assignment of the absolute configuration of all enantiomers of ethyl hydroxy(phenyl)methane(P-phenyl)phosphinate

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Abstract—Ethyl butyryloxy(phenyl)methane(P-phenyl)phosphinate was hydrolyzed using four bacterial species as biocatalysts. In all cases the reaction was stereoselective and isomers bearing an α-carbon atom with an (*S*)-configuration were hydrolyzed preferentially. Also a lack of stereoselectivity toward the phosphorus atom was observed. Hydrolysis of one enantiomeric mixture, namely mixture of (S_P,*R*) and (R_P,*S*) configuration afforded enantiomerically pure ethyl (R_P,*S*)-hydroxy(phenyl)methane(P-phenyl)phosphinate, configuration of which was established by X-ray crystallography. The observed ^{1}H and ^{31}P NMR chemical shifts of Mosher esters of ethyl hydroxy(phenyl)methane(P-phenyl)phosphinate were correlated with the configurations of both stereogenic centers of all four stereoisomers.

1. Introduction

Syntheses of chiral α-hydroxyphosphonates have gathered considerable attention recently mostly due to their usefulness as intermediates for the synthesis of other phosphorus compounds of variable use.[1–4] Hydroxyalkanephosphonic acids have also received attention because their biological activity has not been fully explored. However, isolated examples of their activity include the inhibition of such important medicinal enzymes as renin[5,6] or human immunodeficiency virus (HIV) protease and polymerase.[7–9] Far less data are available about the synthesis of chiral hydroxyphosphinates, especially considering chirality at the phosphorus atom. The only example of the transfer of chirality from the carbon to phosphorus atom was described upon stereoselective lipase-catalyzed acylation of ethyl (1-hydroxyethyl)phenylphosphinate.[10] The same reaction carried out with the use of other lipases have shown, however, a lack of stereoselection at the phosphorus atom.[11] Herein, we have extended the scope of this approach by using microbial cells as biocatalysts for the hydrolysis of ethyl butyryloxy(phenyl)methane(P-phenyl)phosphinate. Some efforts were also undertaken to separate all four stereoisomers of the product—ethyl hydroxy(phenyl)methane(P-phenyl)phosphinate.

2. Results and discussion

2.1. Biotransformations

Racemic ethyl hydroxy(phenyl)methane(P-phenyl)phosphinate **1**, obtained by the classical addition of ethyl phenylphosphinate to benzaldehyde,[12] was converted into ethyl butyryloxy(phenyl)methane(P-phenyl)phosphinate **2** by simple acylation with butyryl chloride. The latter was hydrolyzed using whole cells of four bacterial species (Table 1). As seen from Table 1, the reaction was stereoselective and isomers bearing an α-carbon atom with an (*S*)-configuration were hydrolyzed preferentially with a lack of stereoselectivity toward phosphorus atom (see also Scheme 1). These results are in a good agreement with those observed for ethyl (1-hydroxyethyl)phenylphosphinate.[11]

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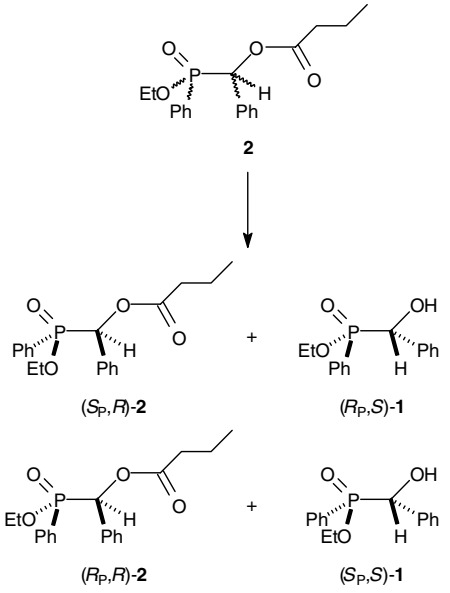
Table 1. Hydrolysis of ethyl butyryloxy(phenyl)methane(P-phenyl)phosphinate **2** by microorganisms via Scheme 1

Microorganism	Time [h]	Conversion [%]		ee of alcohol [%]	
		(R_P,R) (S_P,S)	(S_P,R) (R_P,S)	(S_P,S)	(R_P,S)
Bacillus subtilis	24	49	50	90	90
	72	82	77	24	31
Acinetobacter baumannii	48	33	16	4	33
	72	79	76	19	39
Serratia liquefaciens	90	44	67	51	66
	168	68	63	11	28
Pseudomonas aeruginosa	48	30	14	62	72
	94	41	27	31	38



Scheme 1. Stereochemical course of microbial hydrolysis of racemic ethyl butyryloxy(phenyl)methane(P-phenyl)phosphinate **2**.

The best results were obtained with cells of *Bacillus subtilis* after 24 h reaction time. Although both enantiomeric mixtures were converted in only 50%, the enantiomeric excess of the resulting hydroxyphosphinate **1** was satisfactory. Increasing the reaction time resulted in the elevation of its yield with simultaneous decrease of the stereoselectivity of the process, which is typical for biotransformations carried out with whole cells.

2.2. Resolution of stereoisomers

When purifying ethyl butyryloxy(phenyl)methane(P-phenyl)phosphinate by means of column chromatography, the possibility of the resolution of diastereoisomers, namely a mixture of (R_P,R)-**2** and (S_P,S)-**2** from compounds (S_P,R)-**2** and (R_P,S)-**2**, was noticed. This appeared to be no easy task and we succeeded in only obtaining pure diastereomeric mixture of (S_P,R)-**2** and (R_P,S)-**2** in a 10% yield, when using a silica gel column and mixture of methylene chloride/*n*-hexane/ethyl acetate (1:1:0.5 v/v) as eluent. Efforts to obtain the second diastereomeric mixture, namely the mixture of (R_P,R)-**2** and (S_P,S)-**2**, were unsuccessful.

The diastereomeric mixture of (S_P,R)-**2** and (R_P,S)-**2** was then hydrolyzed using *B. subtilis* as the biocatalyst (17 h; yield 37%; ee 87%) resulting, after HPLC chromatography (preparative C18 column), in pure (R_P,S)-**1** {$[\alpha]_D = +2.8$ (c 1.67, CH_3Cl, 23 °C)}. Crystallization of this compound from methylene chloride/*n*-hexane mixture, carried out in sealed capillary, gave crystals suitable for crystallographic studies. The absolute configuration of this compound was determined by X-ray studies.

2.3. Determination of the absolute configuration of (R_P,S)-1 by X-ray crystallography

The absolute configuration of compound **1**, obtained via biocatalytic hydrolysis of a pure mixture of diastereoisomers of compound **2**, was determined with the Flack parameter refining to a value of 0.01(3). As clearly seen from Figure 1, the configuration of the obtained compound **1** was determined as (R_P,S). This assignment was then used to determine the absolute configuration of the remaining stereoisomers by means of NMR spectroscopy.

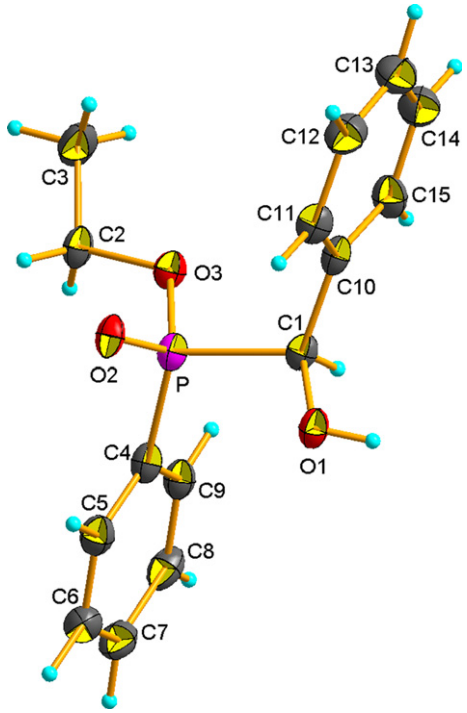


Figure 1. Molecular structure of (R_P,S)-**1** showing the atom-labelling schemes. Displacement ellipsoids are drawn at the 50% probability level.

Compound (R_P,S)-**1** crystallizes from a mixture of methylene chloride/*n*-hexane with one independent molecule in the asymmetric unit (Fig. 1). The molecules are linked by strong hydrogen bonds of the P=O···H–O type formed between phosphinate and hydroxyl moieties of neighboring molecules to give chains extending along the *b* axis. Such chains are linked by weak C–H···O hydrogen bonds

involving phenyl rings and ethyl ester groups. The aforementioned arrangement results in the formation of layers parallel to the *ab* plane. Thus, the hydrophilic core formed by phosphinate fragments is separated by hydrophobic parts formed by all the hydrophobic fragments of the molecule (Fig. 2).

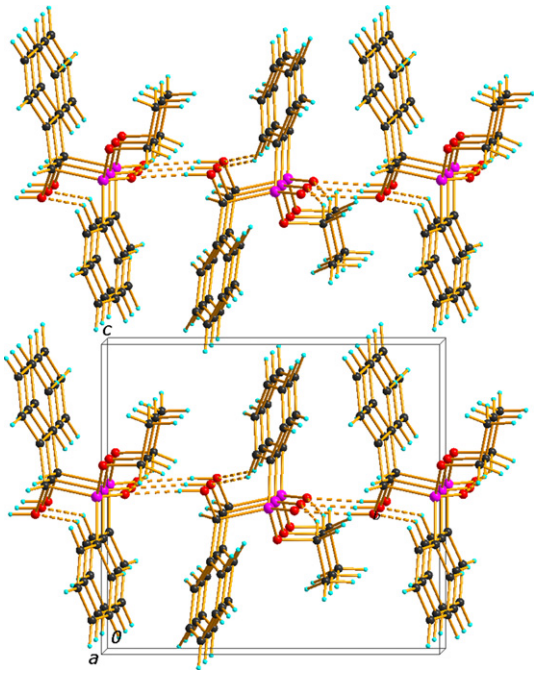
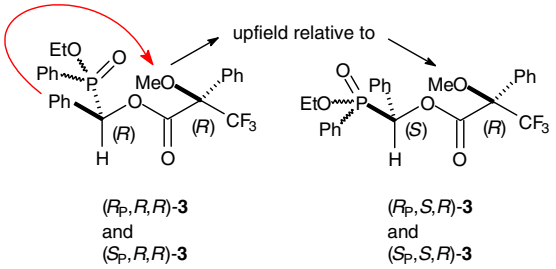


Figure 2. Structural alignment of (R_P,*S*)-**1** molecules in the crystal structure.

2.4. Configurational NMR assignments

NMR is normally used for the determination of absolute configuration of α-hydroxyphosphonates.[1] Since the Mosher approach is most commonly used for that purpose,[13] we have decided to use this approach. In the first step, pure ethyl (R_P,*S*)-hydroxy(phenyl)methane(P-phenyl)-phosphinate was esterified with (*S*)-(+)MTPA-Cl yielding the ester of (*R*)-MTPA (compound (R_P,*S*,*R*)-**3**), thus obtaining the standard for further studies.

In the next step, a non-equimolar mixture of (S_P,*R*)-**2** and (R_P,*S*)-**2** (1:0.47; ee = 36%), obtained as the unreacted substrate isolated from the mixture obtained after hydrolysis of this enantiomeric mixture by *B. subtilis*, was hydrolyzed with small amounts of sulfuric acid in methanol (15 mg of the mixture, three droplets of concentrated sulfuric acid in 3 ml of methanol). This procedure yielded, in a 1:0.47 molar ratio, a mixture of (ee = 36%), which was then acylated with (*S*)-(+)MTPA-Cl resulting in a mixture of compounds (S_P,*R*,*R*)-**3** and (R_P,*S*,*R*)-**3** (molar ratio of 1:0.47) for analysis by means of NMR. The observed chemical shifts of the methoxy protons in the ^{1}H NMR spectra were 3.39 ppm for (S_P,*R*,*R*)-**3** and 3.43 ppm for (R_P,*S*,*R*)-**3**. This is in good agreement with previous studies and results from the anisotropic effect of the phenylphosphinate aromatic ring on the chemical shift of these protons present in the Mosher acid moiety (see Scheme 2).[14]



Scheme 2. Anisotropic effect of the phenyl ring of the phosphinate on chemical shift of the Mosher acid methoxy protons.

In the final step, a mixture of substrate **2** (all four stereoisomers applied in molar ratio of: (R_P,*S*):(S_P,*R*):(R_P,*R*):(S_P,*S*) = 4.6:2.8:1:0.6), available from one experiment of hydrolysis of the 4.6:4.6:1:1 mixture of **2** with *B. subtilis*, was hydrolyzed with sulfuric acid in methanol and the product (a corresponding mixture of four stereoisomers of **1**) acylated with (*S*)-(+)MTPA-Cl. Considering the generality of interaction between phenylphosphinate fragment and the methoxy group in **3**, isomers with an (*S*)-configuration at the α-carbon atom of the phosphinate molecule should have chemical shifts of methoxy protons upfield relative to the corresponding (*R*)-isomers. Therefore, the observed chemical shifts for the remaining (R_P,*R*,*R*)-**3** and (S_P,*S*,*R*)-**3** are 3.42 and 3.50 ppm, respectively.

The same reasoning applies to the ^{31}P NMR spectra. As shown in Scheme 2, the interaction between the phenyl ring and phosphinate group is seen for (S_P,*S*,*R*)-**3** and (R_P,*S*,*R*)-**3** (chemical shifts of 33.00 and 32.80 ppm, respectively) should be upfield relative to isomers (S_P,*R*,*R*)-**3** and (R_P,*R*,*R*)-**3** (32.94 and 32.55 ppm, respectively). This is indeed the fact, which additionally supports proper assignment made by ^{1}H NMR.

3. Experimental

3.1. General

NMR spectra were measured on a Bruker Avance™ 600 at 600.58 MHz for ^{1}H; 243.12 MHz for ^{31}P and 151.02 MHz for ^{13}C in $CDCl_3$ or on a Bruker Avance DRX 300 instrument operating at 300.13 MHz for ^{1}H and 121.50 MHz for ^{31}P in $CDCl_3$. Chemical shifts (δ) are reported in parts per million and coupling constants (*J*) are given in Hertz. ^{1}H NMR are referenced to internal TMS ($\delta = 0.00$), ^{13}C NMR spectra to the center line of $CHCl_3$ ($\delta = 77.23$) and 85% phosphoric acid in H_2O for ^{31}P NMR spectra was used as external reference. Optical rotation was measured in $CHCl_3$ using polAAr-31 polarimeter (578 nm). All compounds were purified by gradient column chromatography using Merck Silica Gel 60 (63–230 mesh) or by HPLC (Varian, Dynamax HPLC Column 250 × 21.4 mm; MICROSORB 300-10 C18). All materials were purchased

from commercial suppliers: Sigma, Aldrich, Fluka, POCh and used without further purification.

3.2. Synthesis of ethyl hydroxy(phenyl)methane-(P-phenyl)phosphinate 1

Aluminum oxide (5 g) was mixed with 5 g of potassium fluoride and powdered in a grinder. Then 20 mmol of ethyl phenylphosphinate and 20 mmol of the acetic aldehyde was added into this mixture and left at room temperature for 48 h. After this time, the mixture was eluted by dichloromethane. The desired compound **1** was purified by gradient column chromatography on silica gel using dichloromethane/ethyl acetate (5:3 v/v) as eluent; R_f (**1**) = 0.29. This procedure resulted in the mixture of diastereoisomers obtained in 1:1 molar ratio with 51% yield.

3.2.1. Mixture of (R_P,*R*)- and (S_P,*S*)-isomers. ^{31}P NMR δ (ppm): 39.56; ^{1}H NMR: δ (ppm) 1.32 (t, $J = 7.0$ Hz, 3H, OCH_3), 3.93–4.18 (m, 2H, OCH_2), 5.16 (d, $J = 10.4$ Hz, 1H, C*H*P), 7.20–7.64 (m, 10H, aromatic protons); ^{13}C NMR δ (ppm): 16.71 (d, $J = 6.1$, *C*H$_3$), 62.09 (O*C*H$_2$), 73.41 (d, $J = 111.3$, *C*HP), 127.18, 127.22, 127.92 (d, $J = 3.1$), 128.08, 128.10, 128.25, 132.68 (d, $J = 2.2$), 132.77, 133.06, 136.58 (aromatic carbons).

3.2.2. Mixture of (R_P,*S*) and (S_P,*R*) isomers. ^{31}P NMR δ (ppm): 38.00; ^{1}H NMR: δ (ppm): 1.27 (t, $J = 7.0$ Hz, 3H, CH_3), 3.93–4.18 (m, 2H, OCH_2), 5.10 (d, $J = 7.4$ Hz, 1H, CHP), 7.20–7.64 (m, 10H, aromatic protons); ^{13}C NMR δ (ppm): 16.69 (d, $J = 5.5$, *C*H$_3$), 62.05 (OCH_2), 73.79 (d, $J = 110.3$, C*H*P), 127.47, 127.50, 128.17, 128.24 (d, $J = 2.4$), 128.38, 128.47, 132.77, 132.83, 133.12, 136.28 (aromatic carbons).

3.3. Synthesis of ethyl butyryloxy(phenyl)methane-(P-phenyl)phosphinate 2

Racemic compound **1** was acylated with butyryl chloride by the following procedure: 10 mmol of compound **1** was added to 100 ml of a mixture containing chloroform and triethylamine (10:1 v/v), followed by the addition of 11 mmol of butyryl chloride. The resulting solution was stirred for 24 h at room temperature and the product purified by means of column chromatography as described above; R_f(**2**) = 0.73. Ethyl butyryloxy(phenyl)methane(P-phenyl)phosphinate (1:1 molar ratio) was obtained with 62% yield.

3.3.1. Mixture of (R_P,*R*)- and (S_P,*S*)-enantiomers. ^{31}P NMR δ (ppm) 34.93; ^{1}H NMR: δ (ppm): 0.87 (t, $J = 7.4$ Hz, 3H, $CH_2CH_2CH_3$), 1.28 (t, $J = 7.1$ Hz, 3H, OCH_2CH_3), 1.55–1.62 (m, 2H, CH_2CH_3), 2.32 (dt, $J = 4.6$ Hz, $J = 7.4$ Hz, 2H, C(O)CH_2), 4.00–4.07 (m, 2H, OCH_2), 6.23 (d, $J = 8.5$ Hz, 1H, C*H*P), 7.25–7.66 (m, 10H, aromatic protons); ^{13}C NMR δ (ppm) 13.71 ($CH_2CH_2CH_3$), 16.68 (d, $J = 5.7$ Hz, OCH_2CH_3), 18.45 ($CH_2CH_2CH_3$), 36.17 (C(O)*C*H$_2$), 62.12 (d, $J = 6.7$ Hz, O*C*H$_2$), 72.99 (d, $J = 117.3$ Hz, *C*HP), 127.76, 127.78, 127.81, 128.41, 128.49, 128.63, 132.64, 132.71, 132.92, 133.48 (aromatic carbons), 172.00 (d, $J = 6.9$ Hz, *C*=O).

3.3.2. Mixture of (R_P,*S*)- and (S_P,*R*)-enantiomers. ^{31}P NMR δ (ppm) 34.52; ^{1}H NMR: δ (ppm): 0.83 (t, $J = 7.4$ Hz, 3H, $CH_2CH_2CH_3$), 1.25 (t, $J = 7.0$ Hz, 3H, OCH_2CH_3), 1.50–1.58 (m, 2H, CH_2CH_3), 2.27 (dt, $J = 2.2$ Hz, $J = 7.4$ Hz, 2H, C(O)CH_2), 4.00–4.07 (m, 2H, OCH_2), 6.32 (d, $J = 10.6$ Hz, 1H, C*H*P), 7.25–7.72 (m, 10H, aromatic protons); ^{13}C NMR δ (ppm): 13.63 ($CH_2CH_2CH_3$), 16.58 (d, $J = 6.3$ Hz, OCH_2CH_3), 18.45 ($CH_2CH_2CH_3$), 36.17 (C(O)*C*H$_2$), 61.91 (d, $J = 6.6$ Hz, O*C*H$_2$), 72.35 (d, $J = 119.1$ Hz, *C*HP), 127.99, 128.02, 128.41 (2C), 128.49, 128.62, 132.65, 132.71, 133.90, 133.37 (aromatic carbons), 171.94 (d, $J = 7.5$, *C*=O).

3.4. Synthesis of Mosher esters

Compound **1** of various stereomeric compositions was acylated according to the literature:[13] 0.10 mmol of **1** was dissolved in the mixture composed of dry dichloromethane (300 μl) and dry pyridine (300 μl), followed by the addition of 0.14 mmol of (*S*)-(+)MTPA-Cl. The mixture was left for 3 days at room temperature. An excess of 3-dimethylamino-1-propylamine (0.20 mmol) was then added and after 5 min at room temperature, the mixture was diluted with diethyl ether (10 ml), washed by cold dilute HCl (10 ml) and water (10 ml), and dried over anhydrous magnesium sulfate. After filtration of the drying agent, ether was evaporated, compound **3** was purified by means of HPLC (C-18 column; gradient: from 60% of acetonitrile in water to 100% of acetonitrile; retention time of **3**: 13.6 min).

3.5. Microorganisms: growth and biotransformation conditions

The strains of *Pseudomonas aeruginosa*, *Bacillus subtilis*, *Serratia liquefaciens* and *Acinetobacter baumannii* were taken from our own collection. Their taxonomy was previously analyzed by Deutsche Sammlung für Mikroorganismen und Zellkulturen, Braunschweig, Germany. In order to achieve the most vigorous growth accompanied by the best lipolytic activity, several media were tested and the one of choice is composed of: 10 g of starch soluble, 1 g of yeast extract, 5 g of $(NH_4)_2SO_4$, 2 g of K_2HPO_4, 100 μl of tributyrin and 1000 ml of distilled water. Microorganisms were incubated for 3 days at 26 °C with shaking at 150 rpm. The cells were then centrifuged at 3000 rpm for 10 min and washed twice in 0.017 M phosphate buffer, pH 7.0.

Biotransformations were performed in 100 ml of 0.017 M phosphate buffer, pH 7.0 supplied with 50 μl of substrate. The samples were shaken at 150 rpm at room temperature. After the process, biomases were centrifuged, the supernatant extracted twice with ethyl acetate and dried over anhydrous magnesium sulfate. After filtration, organic solvent was evaporated and the reaction progress and stereoselectivity analyzed by ^{31}P NMR using quinine as a chiral discriminator.[15]

3.6. Crystal structure of (R_P,S)-hydroxy(phenyl)methane-(P-phenyl)phosphinate

X-ray data were collected from a single colorless plate, $0.08 \times 0.21 \times 0.26$ mm, at 100 K using graphite-monochromated Cu K_α ($\lambda = 1.5418$ Å) radiation on a Xcalibur PX diffractometer (ω- and φ-scan). The instrument was equipped with Oxford Cryosystems low-temperature devices. The data was numerically corrected for absorption with the use of CRYSALIS RED 1.171, the Xcalibur PX Software.[16] The structure was solved by direct methods using the SHELXS-97 program[17] and refined by full-matrix least-squares calculations on F^2 with SHELXL-97.[18] Non-hydrogen atoms were refined with anisotropically thermal parameters. The H atoms bound to C atoms were included in geometrically calculated positions, with the C–H distances in the range 0.95–1.00 Å, and refined using riding model, with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl and $1.2U_{eq}(C)$ for the remainder. The hydroxyl H atom was located in the difference Fourier map and subsequently treated as a rigid rotating group with the O–H distance of 0.84 Å and with $U_{iso}(H) = 1.5U_{eq}(O)$. The absolute configuration of **1** was determined with the Flack parameter refining to a value of 0.01(3). The asymmetric unit of the crystal consists of one compound **1** molecule: $C_{15}H_{17}O_3P$, $M_r = 276.26$, monoclinic, space group $P2_1$, $a = 6.090(2)$, $b = 11.418(4)$, $c = 10.488(4)$ Å, $\beta = 93.85(3)°$, $V = 727.6(4)$ Å^3, $d_{calc} = 1.261$, $F(000) = 292$, $\mu = 1.691$ mm^{-1}, $T_{min} = 0.658$, $T_{max} = 0.900$, $Z = 2$, 5606 measured reflections ($-7 \leqslant h \leqslant 7$, $-11 \leqslant k \leqslant 14$, $-11 \leqslant l \leqslant 12$), 2268 independent and 2160 observed reflections with $I > 2\sigma(I)$ ($R_{int} = 0.0753$), 174 parameters, $R = 0.0583$, $wR_2 = 0.1541$ for all reflections, $w = 1/[\sigma^2(F^2) + (0.1180P)^2 + 0.2325P]$ where $P = (F_o^2 + 2F_c^2)/3$.

CCDC 619249 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336033; e-mail: deposit@ccdc.cam.uk).

Acknowledgements

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References

1. Kolodiazhnyi, O. I. *Tetrahedron: Asymmetry* **2005**, *16*, 3295.
2. Plażuk, D.; Zakrzewski, J.; Rybarczyk-Pirek, A. *Tetrahedron: Asymmetry* **2006**, *17*, 1975.
3. Pawar, V. D.; Bettigeri, S.; Weng, S.-S.; Kao, J. Q.; Chen, C.-T. *J. Am. Chem. Soc.* **2006**, *128*, 6308.
4. Nesterov, V. V.; Kolodiazhnyi, O. I. *Zh. Obsch. Khim.* **2005**, *75*, 1225.
5. Patel, D. V.; Rielly-Gauvin, K.; Ryono, D. E. *Tetrahedron Lett.* **1990**, *31*, 5587.
6. Patel, D. V.; Rielly-Gauvin, K.; Ryono, D. E.; Free, C. S.; Rogers, W. L.; Smith, S. A.; DeForrest, J. M.; Oehl, R. S.; Petrillo, E. W., Jr. *J. Med. Chem.* **1995**, *38*, 4557.
7. Stowasser, B.; Budt, K. H.; Jian-Qi, L.; Peyman, A.; Ruppert, D. *Tetrahedron Lett.* **1992**, *33*, 6625.
8. Yokomatsu, T.; Yamagishi, T.; Shibuya, S. *Tetrahedron: Asymmetry* **1993**, *4*, 1401.
9. Srinivas, R.; Comnnely, M.; Fidland, A. *Antivir. Res.* **1987**, *35*, 23.
10. Shioji, K.; Tashiro, A.; Shibata, S.; Okuma, K. *Tetrahedron Lett.* **2003**, *44*, 1103.
11. Majewska, P.; Lejczak, B.; Kafarski, P. *Tetrahedron: Asymmetry*, submitted for publication.
12. Texier-Boullet, F.; Lequitte, M. *Tetrahedron Lett.* **1986**, *27*, 3515.
13. Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512.
14. Eidenhammer, G.; Hammerschmidt, F. *Synthesis* **1996**, 748.
15. Żymańczyk-Duda, E.; Skwarczyński, M.; Lejczak, B.; Kafarski, P. *Tetrahedron: Asymmetry* **1996**, *7*, 1277.
16. Oxford Diffraction Ltd. (1995–2003). Xcalibur PX Software—CryAlis CCD and CrysAlis RED Version 1.171. Oxford Diffraction Poland, Wrocław, Poland.
17. Sheldrick, G. M. SHELXS-97. *Program for the Solution of Crystal Structures*; University of Göttingen: Germany, 1997.
18. Sheldrick, G. M. SHELXL-97. *Program for the Refinement of Crystal Structures*; University of Göttingen: Germany, 1997.