Lipase YS-Catalyzed Enantioselective Transesterification of Alcohols of Bicarbocyclic Compounds

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Lipase YS-catalyzed enantioselective acylations of (1*RS*, 2*RS*, 4*RS*, 5*RS*)-bicyclo[2.2.1]heptane-2,5-diol, (1*RS*, 2*SR*, 4*RS*, 5*SR*)-bicyclo[2.2.2]octane-2,5-diol, (1*RS*, 2*RS*, 4*RS*, 5*RS*)-bicyclo[2.2.2]octane-2,5-diol, and (1*RS*, 2*SR*, 5*RS*, 6*SR*)-bicyclo[3.3.1]nonane-2,6-diol with aryl acetates such as phenyl acetate, 1-naphthyl acetate, and 2-naphthyl acetate gave the monoacetates and the diols in optically active forms. The optical purities of (+)-(2*R*, 5*R*)-2-acetoxybicyclo[2.2.1]heptan-5-ol, (−)-(1*S*, 2*R*, 4*S*, 5*R*)-2-acetoxybicyclo[2.2.2]octan-5-ol, and (+)-(2*R*, 6*R*)-2-acetoxybicyclo[3.3.1]nonan-6-ol obtained using phenyl acetate were higher than those of the monoacetates which have been resolved by PLE-catalyzed hydrolysis of the corresponding racemic diacetates. Enzymic acylations of the diols using phenyl esters such as phenyl propanoate, phenyl butanoate, and phenyl octanoate as acylating agents gave the corresponding monoesters, which showed nearly the same enantiomeric excess value as the acetates. A simple model for predicting which enantiomer of racemic alcohols is acylated preferentially by lipase YS-catalyzed enantioselective transesterification is proposed on the basis of the results obtained here.

The immense potential of hydrolytic enzymes as chiral catalysts in organic reactions is well-documented.[1] Lipase and esterase are especially useful for organic synthesis, because they can function in nonaqueous media.[2] A large number of papers have described the preparation of chiral synthons by lipase and esterase-catalyzed transesterification in organic solvents, and enol acetates are often employed as an acylating agent to make an enzymic transesterification essentially irreversible.[3] However, the use of enol-esters for the enzyme-catalyzed acylation has the disadvantage of side reactions caused by the aldehyde originating from the enol.[4] Thus, we examined lipase-catalyzed transesterifications of diols by using some aryl esters as acyl donors.

Recently, we have prepared optically active diols of bicyclo[2.2.1]heptane,[5] bicyclo[2.2.2]octane,[5] and bicyclo[3.3.1]nonane,[6] via pig liver esterase (PLE)-catalyzed hydrolysis of the racemic diacetates. Although some of them are currently undergoing investigation as chiral ligands of organometallic catalysts[7] and as chiral subunits for constructing optically active crown ethers,[6] the enantiomeric excess (e.e.) values of some diols were unsatisfactory. We now report an improvement in the optical purities of these diols by lipase YS-catalyzed transesterification of the racemic diols. In order to promote further progress towards a final formulation of an accurate active-site model of lipase YS, we propose a simple model for predicting which enantiomer of racemic alcohols is acylated preferentially by this enzyme.

Results and Discussion

We employed six aryl esters (1-naphthyl acetate, 2-naphthyl acetate, phenyl acetate, phenyl propanoate, phenyl butanoate, and phenyl octanoate) as acylating agents, because they are more stable than enol ester in organic solvents and the resulting alcohols do not cause side reactions. Enantioselective acylations of racemic diols were carried out in dry diisopropyl ether or dry cyclohexane in the presence of a cosolvent, dry tetrahydrofuran, because lipase YS (lipase from *pseudomonus sp.*) was easily dispersed in these media and the cosolvent overcame solubility problems of the substrate. Alterations of the solvent did not influence the stereoselectivity of the acylations examined here. The progress of the reaction was monitored by GLC and the reaction was terminated at about 50% conversion by filtration of the enzyme. The absolute configurations and the maximum rotations of all diols and acetates described here have been reported in our recent papers.[5,6] The absolute configurations and the e.e. values of the other ester were determined by their conversions into the corresponding diols followed by comparison of the specific rotations of the diols with the known value.[5,6]

First, the acylations of the diols were carried out using vinyl acetate and aryl (phenyl, 1-naphthyl, and 2-naphthyl) acetates, and the results are summarized in Table 1. Although the acylations with naphthyl acetates proceeded a little slowly, the rate of the acylation with phenyl acetate was comparable to that with vinyl acetate. So far as the acylating agents employed here are concerned, the difference in the enantioselectivity of the reactions caused by alteration in the alcohol moieties of the acylating agent can not be regarded as significant.

Recently, we prepared the monoacetates (−)-**2**, (+)-**4**, and (+)-**9** in 19%, 21%, and 30% e.e., respectively, by PLE-catalyzed hydrolysis of the corresponding diacetates.[5,6] As can be seen in Table 1, lipase YS-catalyzed transesterification with phenyl acetate improved the optical purities of (+)-**2**, (−)-**4**, and (+)-**9** to 51, 66, and 99% e.e., respectively, whereas the optical purity of (+)-**7** (84% e.e.)[5] resolved by PLE-catalyzed hydrolysis was higher than that of (−)-**7** obtained by

Table 1. Lipase YS-Catalyzed Enantioselective Acylations of Racemic Diols

Diol	Acylating agent	Time (h)	Products	% yield	% e.e.	$[\alpha]_D$/°
(±)-**1**	Vinyl acetate	28	(−)-(2*S*,5*S*)-**1**	50	25	−1.70[a]
			(+)-(2*R*,5*R*)-**2**	39	35	+9.51[b]
(±)-**1**	Phenyl acetate	24	(−)-(2*S*,5*S*)-**1**	50	35	−2.38[a]
			(+)-(2*R*,5*R*)-**2**	41	51	+13.9[b]
(±)-**1**	1-Naphthyl acetate	44	(−)-(2*S*,5*S*)-**1**	42	51	−3.47[a]
			(+)-(2*R*,5*R*)-**2**	54	30	+8.15[b]
(±)-**1**	2-Naphthyl acetate	46	(−)-(2*S*,5*S*)-**1**	50	41	−2.79[a]
			(+)-(2*R*,5*R*)-**2**	48	44	+11.9[b]
(±)-**3**	Vinyl acetate	46	(+)-(2*S*,5*S*)-**3**	43	53	+24.1[a]
			(−)-(2*R*,5*R*)-**4**	54	65	−21.7[b]
(±)-**3**	Phenyl acetate	30	(+)-(2*S*,5*S*)-**3**	49	63	+28.8[a]
			(−)-(2*R*,5*R*)-**4**	47	66	−22.0[b]
(±)-**3**	1-Naphthyl acetate	35	(+)-(2*S*,5*S*)-**3**	49	40	+18.3[a]
			(−)-(2*R*,5*R*)-**4**	45	39	−12.9[b]
(±)-**3**	2-Naphthyl acetate	44	(+)-(2*S*,5*S*)-**3**	36	53	+24.2[a]
			(−)-(2*R*,5*R*)-**4**	31	65	−21.6[b]
(±)-**3**	Phenyl butanoate	68	(+)-(2*S*,5*S*)-**3**	47	75	+34.2[a]
			(−)-(2*R*,5*R*)-**5**	47	67	−13.1[b]
(±)-**6**	Vinyl acetate	122	(+)-(2*S*,5*S*)-**6**	47	14	+7.34[a]
			(−)-(2*R*,5*R*)-**7**	39	26	−6.24[b]
(±)-**6**	Phenyl acetate	69	(+)-(2*S*,5*S*)-**6**	48	19	+9.99[a]
			(−)-(2*R*,5*R*)-**7**	33	28	−6.56[b]
(±)-**6**	1-Naphthyl acetate	72	(+)-(2*S*,5*S*)-**6**	46	18	+9.32[a]
			(−)-(2*R*,5*R*)-**7**	45	23	−5.47[b]
(±)-**6**	2-Naphthyl acetate	94	(+)-(2*S*,5*S*)-**6**	31	21	+11.4[a]
			(−)-(2*R*,5*R*)-**7**	38	30	−7.10[b]
(±)-**8**	Vinyl acetate	21	(−)-(2*S*,6*S*)-**8**	51	73	−47.5[a]
			(+)-(2*R*,6*R*)-**9**	42	98	+63.7[b]
(±)-**8**	Phenyl acetate	18	(−)-(2*S*,6*S*)-**8**	47	80	−52.1[a]
			(+)-(2*R*,6*R*)-**9**	39	99	+63.8[b]
(±)-**8**	1-Naphthyl acetate	20	(−)-(2*S*,6*S*)-**8**	53	76	−49.2[a]
			(+)-(2*R*,6*R*)-**9**	43	94	+61.2[b]
(±)-**8**	2-Naphthyl acetate	39	(−)-(2*S*,6*S*)-**8**	50	95	−61.5[a]
			(+)-(2*R*,6*R*)-**9**	44	95	+61.8[b]
(±)-**8**	Phenyl propanoate	23	(−)-(2*S*,6*S*)-**8**	54	69	−44.4[a]
			(+)-(2*R*,6*R*)-**10**	41	97	+63.7[b]
(±)-**8**	Phenyl butanoate	70	(−)-(2*S*,6*S*)-**8**	45	67	−43.3[a]
			(+)-(2*R*,6*R*)-**11**	43	80	+44.5[b]
(±)-**8**	Phenyl octanoate	74	(−)-(2*S*,6*S*)-**8**	48	62	−39.9[a]
			(+)-(2*R*,6*R*)-**12**	39	88	+37.3[b]

a) In MeOH, b) In $CHCl_3$.

lipase YS-catalyzed transesterification of (±)-**6**. In regard to the stereoselectivity of the reaction, lipase YS-catalyzed transesterifications of the diols (±)-**1**, (±)-**3**, and (±)-**6** gave the enantiomers of the monoacetates **2**, **4**, and **7** obtained by PLE-catalyzed hydrolyses of the corresponding diacetates, whereas the acylation of (±)-**8** gave the same monoacetate (+)-**9** as PLE-catalyzed hydrolysis (Chart 1).

Next, we carried out acylations of the diols using phenyl esters as acylating agents to prepare the monoesters such as propanoate, butanoate, and octanoate, the results being given in Table 1. Although the reaction rate cleary decreased with increasing length of acyl residues from acetyl to octanoyl in acyl donors, the monoesters isolated showed nearly the same e.e. value as the corresponding monoacetate.

In order to obtain further information on the stereoselectivity of lipase YS-catalyzed acylation, bicyclic alcohols (±)-**13**, (±)-**15**, and (±)-**17** were acylated with isopropenyl acetate and the results are given in Table 2 (Chart 2). Recently, Meltz and Saccomano[9] have published porcine pancreatic lipase (PPL)-mediated acylation of bicyclic alcohols. The PPL-catalyzed acylations of (±)-**15** and (±)-**17** with 2,2,2-trichloroethyl butanoate gave (−)-(2*S*)-**15** and (−)-(2*S*)-**17**, respectively, but the acylation of (±)-**13** provided optically

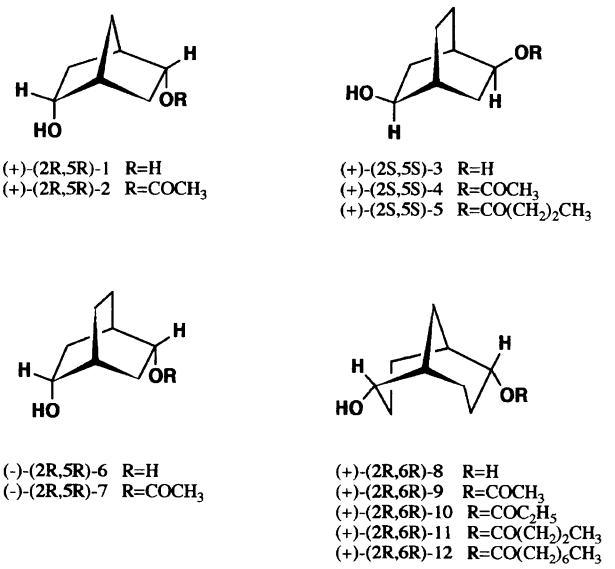


Chart 1.

inactive products regardless of the extent of conversion. On the other hand, all alcohols were resolved to give (−)-(2*S*)-**13**, (−)-(2*S*)-**15**, and (−)-(2*S*)-**17** by lipase YS-catalyzed acylation.

Recent interest in the synthetic potential of lipases has led to models to predict their stereoselectivity usually based on either the size or hydrophobicity of the groups at the stereocenter.[8] The enzymic acylation of substrates having a rigid framework such as the bicyclic compounds studied here provides valid information which will be used to develop an active site model of lipase YS. Based on the sizes of the groups at the asymmetric center, the stereospecificity of the acylations presented in this paper can be summarized in a simple model (Fig. 1). This is a rule to predict which enantiomer of racemic alcohols reacts faster in the enantioselective transesterification catalyzed by lipase YS.

This rule is not only applicable for substrates possessing a bicyclic framework but also rationalizes the enantiotopic selectivity in lipase YS-catalyzed acylations of (±)-spiro[4.4]nonane-1,6-diol and (±)-3,3-dimethyl-1,2-butanediol with isopropenyl acetate giving (−)-(1*R*,5*S*,6*R*)-1-acetoxyspiro[4.4]nonan-6-ol[10] and (+)-(2*S*)-2-acetoxy-3,3-dimethyl-1-butanol, respectively.

As mentioned here, lipase YS-catalyzed acylations of diols (±)-**1**, (±)-**3**, and (±)-**8** gave the monoacetates (+)-(2*R*,5*R*)-**2**, (−)-(2*R*,5*R*)-**4**, and (+)-(2*R*,6*R*)-**9**, the optical purities of which were improved compared to those of the monoacetates resolved by PLE-catalyzed hydrolyses of the corresponding racemic diacetates. The enzymic transesterifications of racemic diols with phenyl esters proceeded at a rate acceptable for preparative purposes and phenyl esters can be employed as acylating agents for the preparation of a variety of optically active esters.

Experimental

Optical rotations were measured using a JASCO DIP-40 polarimeter. Gas chromatography was performed on a Simadzu GS 8A chromatograph using an SE-52 on Uniport HP, 2 m ×2.6 mm column and a PEG 20M on Chromosorb W, 2 m ×2.6 mm column. The racemic diols **1**,[11] **3**,[12] **6**,[12] and **8**[13] were prepared according to the literature procedures and the optically active products isolated were identified by comparing their infrared and ^{1}H NMR spectra and retention times in gas chromatography with those of the racemic authentic samples. Lipase YS was supplied by Amano Pharmaceutical Co. and used without further purification.

(1*RS*,2*RS*,4*RS*,5*RS*)-Bicyclo[2.2.1]heptane-2,5-diol ((±)-*endo,endo*-diol) (1). According to the known procedure,[11] reduction of (±)-bicyclo[2.2.1]heptane-2,5-dione (3.10 g, 25.0 mmol) with lithium tri-*t*-butoxyhydridoaluminate in dry THF gave (±)-**1** (2.08 g, 65% yield), mp 228—229°C (lit,[11] mp 229—230°C) after recrystallization from diethyl ether–pentane.

(1*RS*,2*SR*,4*RS*,5*SR*)-Bicyclo[2.2.2]octane-2,5-diol ((±)-*exo,exo*-diol) (3) and (1*RS*,2*RS*,4*RS*,5*RS*)-Bicyclo[2.2.2]octane-2,5-diol ((±)-*endo,endo*-diol) (6). Reduction of (±)-bicyclo[2.2.2]octane-2,5-dione (5.30 g, 38.4 mmol) with $LiAlH_4$ in dry diethyl ether gave a mixture of (±)-**3**, (±)-**6**, and its *endo,exo*-isomer, which was chromatographed on silica gel (eluted with $CHCl_3$/EtOH, 9/1) to give (±)-**6**, mp 280—283°C (in a sealed tube) (eluted first) (715 mg, 13% yield) and (±)-**3**, mp 269—271°C (in a sealed tube) (eluted subsequently) (820 mg, 15% yield). Their structures were identified by comparing the IR and ^{1}H NMR spectra of the diols (±)-**3** and (±)-**6** and their diacetates with those described in the literature.[12]

(1*RS*,2*SR*,5*RS*,6*SR*)-Bicyclo[3.3.1]nonane-2,6-diol ((±)-*endo,endo*-diol) (8). Reduction of (±)-bicyclo[3.3.1]nonane-2,6-dione with $LiAlH_4$ in dry diethyl ether gave (±)-**8** (9.31 g, 84% yield), mp 219—220°C (Lit,[13] mp 219°C) after recrystallization from ethyl acetate.

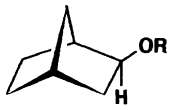
Representative Procedure for Lipase YS-Catalyzed Transesterification of Alcohols with Enol Acetate. To a solution of (±)-**1** (200 mg, 1.56 mmol) and vinyl acetate (1.34 g, 15.6 mmol) in dry diisopropyl ether (50 ml) and dry THF (2 ml) was added lipase YS (1.3 g) and then the mixture was stirred for 28 h at 30°C. After the lipase was removed by filtration, the solution was concentrated in vacuo. Silica gel chromatography of the product gave the monoacetate (+)-(2*R*,5*R*)-2-acetoxybicyclo[2.2.1]-heptan-5-ol (**2**) (eluted with benzene/diethyl ether 85/15), $[\alpha]_D^{27}$ +9.51° (*c* 2.83, $CHCl_3$), (103 mg, 39% yield) and (−)-(2*S*,5*S*)-**1** (eluted with diethyl ether), $[\alpha]_D^{27}$ −1.70° (*c* 4.05, methanol), (100 mg, 50% yield).

Representative Procedure for Lipase YS-Catalyzed Transesterification of Diols with Phenyl Acetate. To a solution of (±)-**8** (200 mg, 1.28 mmol) and phenyl acetate (870 mg, 6.40 mmol) in dry cyclohexane (50 ml) and dry THF (20 ml) was added lipase YS (600 mg). After 18 h of incubation, the enzyme was filtered off and the solvent was removed in vacuo. Silica-gel chromatography of the residue gave an excess of phenyl acetate and phenol (eluted with benzene), (+)-(2*R*,6*R*)-**9** (eluted with benzene/diethyl ether 8/2), $[\alpha]_D^{26}$ +63.8° (*c* 1.15, $CHCl_3$)

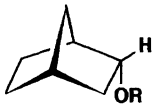
Table 2. Lipase YS-Catalyzed Enantioselective Acylations of Racemic Alcohols

Alcohol	Acylating agent	Time (h)	Products	% yield	% e.e.	$[\alpha]_D$/°
(±)-**13**	Isopropenyl acetate	45	(−)-(2*S*)-**13**	46	17	−0.61[a]
			(−)-(2*R*)-**14**	45	19	−2.17[a]
(±)-**15**	Isopropenyl acetate	89	(−)-(2*S*)-**15**	52	63	−1.20[a]
			(+)-(2*R*)-**16**	40	90	+12.7[a]
(±)-**17**	Isopropenyl acetate	312	(+)-(2*S*)-**17**	48	45	+14.1[a]
			(−)-(2*R*)-**18**	48	47	−9.31[a]

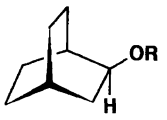
a) In $CHCl_3$.



(-)-(2S)-13 R=H
(+)-(2S)-14 R=$COCH_3$



(+)-(2R)-15 R=H
(+)-(2R)-16 R=$COCH_3$



(+)-(2S)-17 R=H
(+)-(2S)-18 R=$COCH_3$

Chart 2.

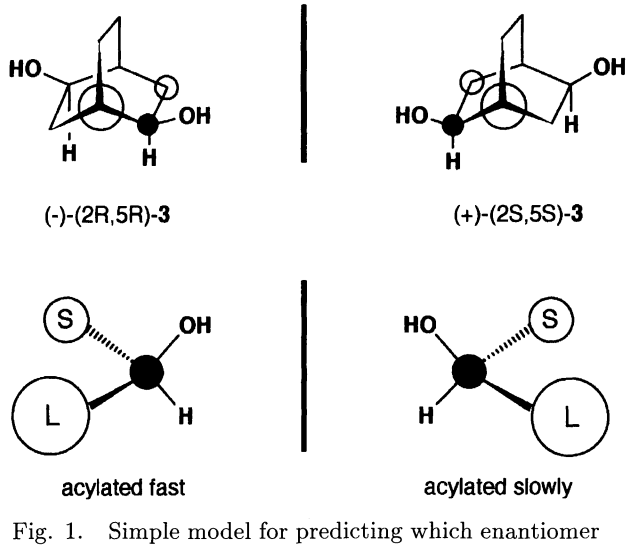


Fig. 1. Simple model for predicting which enantiomer of racemic alcohols is acylated preferentially by lipase YS-catalyzed enantioselective transesterification.

(99 mg, 39% yield), and (−)-(2*S*,6*S*)-**8** (eluted with diethyl ether), $[\alpha]_D^{25}$ −52.1° (*c* 0.900, methanol) (94 mg, 47% yield).

Representative Procedure for Lipase YS-Catalyzed Transesterification of Diols with Naphthyl Acetate. To a solution of (±)-**6** (150 mg, 1.05 mmol) and 2-naphthyl acetate (977 mg, 5.25 mmol) in dry cyclohexane (50 ml) and dry THF (10 ml) was added lipase YS (400 mg) and the mixture was stirred for 94 h at 30°C. After the lipase was filtered off, the solvent was removed in vacuo. Silica-gel chromatography of the product gave an excess of 2-naphthyl acetate and naphthol (eluted with benzene), (−)-(2*R*,5*R*)-**7** (eluted with benzene/diethyl ether 9/1), $[\alpha]_D^{26}$ −7.10° (*c* 0.850, $CHCl_3$), (74 mg, 38% yield), and (+)-(2*S*,5*S*)-**6** (eluted with diethyl ether), $[\alpha]_D^{27}$ +11.4° (*c* 1.10, MeOH), (46 mg, 31% yield).

Representative Procedure for Lipase YS-Catalyzed Transesterification of Diols with Phenyl Esters (Propanoate, Butanoate, and Octanoate). To a solution of (±)-**8** (200 mg, 1.28 mmol) and phenyl butanoate (1.05 g, 6.40 mmol) in dry cyclohexane (50 ml) and dry THF (20 ml) was added lipase YS (500 mg) and the mixture was stirred for 70 h at 30°C. After removal of the lipase and the solvent, the residue was chromatographed on silica gel to give recovered phenyl butanoate and phenol (eluted with benzene), (+)-(2*R*,6*R*)-2-(butanoyloxy)bicyclo[3.3.1]-nonan-6-ol (**11**) (eluted with benzene/diethyl ether 9/1), $[\alpha]_D^{20}$ +44.5° (*c* 0.838, $CHCl_3$), (124 mg, 43% yield), and (−)-(2*S*,6*S*)-**8** (eluted with diethyl ether/methanol 49/1), $[\alpha]_D^{20}$ −43.3° (*c* 0.851, methanol), (90 mg, 45% yield).

Representative Procedure for Lithium Aluminum Hydride Reduction of Esters. A solution of (+)-(2*R*,6*R*)-**11**, $[\alpha]_D$ +44.5°, (67 mg, 0.30 mmol) in dry diethyl ether (20 ml) was added to a suspension of $LiAlH_4$ (23 mg, 0.61 mmol) in dry diethyl ether (10 ml) and the mixture was heated under reflux for 6 h. To the chilled reaction mixture was added an aqueous solution of ammonium chloride with ice cooling and an inorganic solid was removed by filtration. After the filtrate was worked up as usual, preparative silica-gel TLC of the product gave (+)-(2*R*,6*R*)-**8**, $[\alpha]_D^{20}$ +51.8° (*c* 0.398, methanol), (35 mg, 75% yield).

LiAlH4 Reduction of (+)-5. By a manner similar to that described above, (−)-(2*R*,5*R*)-**3**, $[\alpha]_D^{22}$ −30.6° (*c* 1.55, methanol) was prepared from (−)-(2*R*,5*R*)-**5**, $[\alpha]_D$ −13.1° ($CHCl_3$).

$LiAlH_4$ Reduction of (+)-10. By a manner similar to that described above, reduction of (+)-(2*R*,6*R*)-**10**, $[\alpha]_D$ +63.7° ($CHCl_3$) gave (+)-(2*R*,6*R*)-**8**, $[\alpha]_D^{26}$ +62.5° (*c* 2.05, methanol).

$LiAlH_4$ Reduction of (+)-12. By a manner similar to that described above, reduction of (+)-(2*R*,6*R*)-**12**, $[\alpha]_D$ +37.3° ($CHCl_3$) gave (+)-(2*R*,6*R*)-**8**, $[\alpha]_D^{27}$ +56.7° (*c* 1.95, methanol).

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