N-Acetyl-D-phenylalanine Methyl Ester (3b). Isolated yield of crude, 302 mg, 55%, for reaction in water and 264 mg, 48%, for reaction in reverse micelles: mp 88.2 °C (lit.[20] mp 89.5–90 °C); $[\alpha]^{25}_D$ −19.3° (c = 1, methanol) (lit.[20] $[\alpha]^{25}_D$ −19°); ee >99% as determined by ^1H NMR using [Eu(tfc)$_3$]; TLC, chloroform–methanol (9:1), R_f = 0.66.

N-Acetyl-DL-alanine methyl ester (1c) was prepared from DL-alanine as described for **1a**: bp 76 °C (0.2 mm); ^1H NMR (300 MHz $CDCl_3$) δ 6.11 (br s, 1 H, NH), 4.58–4.65 (q, 1 H, CH, J = 7.27 Hz), 3.76 (s, 3 H, OCH_3), 2.02 (s, 3 H, $COCH_3$), 1.41 (d, 3 H, CH_3 J = 7.2 Hz). Anal. Calcd for $C_6H_{11}NO_3$: C, 49.65; H, 7.59; N, 9.65. Found: C, 49.62; H, 7.67; N, 9.56.

N-Acetyl-L-alanine (2c) was obtained by reaction of **1c** (1.45 g, 10 mmol) with yeast cells (10 g, wet) in 100 mL of solvent. Isolated yield of crude, 522 mg, 72%, for reaction in water and 470 mg, 65%, for reaction in reverse micelles: mp 122–123 °C (lit.[21] mp 115–128 °C); $[\alpha]^{25}_D$ −57.3° (c = 1, water) (lit.[21] $[\alpha]^{25}_D$ −59.7°); ^1H NMR (300 MHz, $CDCl_3$, DMSO-d_6) δ 7.16 (br s, 1 H, NH), 4.36–4.55 (q, 1 H, CH, J = 7.2 Hz), 1.98 (s, 3 H, $COCH_3$), 1.39 (d, 3 H, CH_3 J = 7.2 Hz).

N-Acetyl-D-alanine Methyl Ester (3c). Isolated yield of crude, 378 mg, 52%, for reaction in water and 290 mg, 40%, for reaction in reverse micelles: $[\alpha]^{25}_D$ +90.1° (c = 1, water) (lit.[22] $[\alpha]^{25}_D$ +89.4°); ee >99% as determined by ^1H NMR using [Eu(tfc)$_3$]; TLC, chloroform–methanol (9:1) R_f = 0.55.

Acknowledgment. We thank CSIR, New Delhi, for financial assistance and Dr. A. V. Rama Rao, Director, RRL-Hyderabad, for his encouragement.

Registry No. **1a**, 36061-00-4; **1b**, 62436-70-8; **1c**, 26629-33-4; **2a**, 42429-20-9; **2b**, 2018-61-3; **2c**, 97-69-8; **3a**, 36060-85-2; **3b**, 21156-62-7; **3c**, 19914-36-4; bis(2-ethylhexyl) sulfosuccinate sodium salt, 577-11-7.

Synthesis of the Pheromone Components of the Grape Borer *Xylotrechus pyrrhoderus* by Microbiological Reduction of an α-Diketone†

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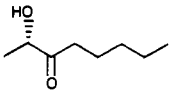
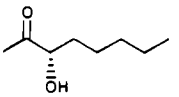
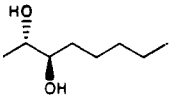
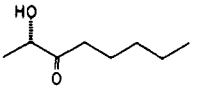
In a continuation of our investigation on the preparation of chiral hydroxy synthons by microbial reduction of the corresponding mono- or diketones,[1-3] we have carried out a study on the reduction of α-diketones. Enzymatic or microbiological reductions of α-diketones have already been studied, mostly on substituted benzils or benzoins[4-7] and α,β-diketodithianes,[8] and α-hydroxy ketones have been reduced in the same manner to obtain optically active α-diols,[9-11] but to our knowledge, no systematic investigation on the microbiological reduction of acyclic α-diones has been published. We started such a study on various acyclic α-diones. Resting cells able to reduce these compounds were screened from our stock cultures of bacteria, yeasts, and fungi, and none of them failed. Either or both carbonyl groups can be reduced, and thus various isomers and stereoisomers of α-hydroxy ketones and α-diols were obtained, as will be described elsewhere.

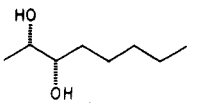
This paper reports on the microbiological reduction of one particular α-diketone, octane-2,3-dione, that enabled us to obtain the two components of a natural pheromone in an efficient two-step chemoenzymatic synthesis. The male sex pheromone of an important pest of Japanese vineyards, the grape borer *Xylotrechus pyrrhoderus*, has been identified as a mixture of (+)-(2S)-2-hydroxyoctan-3-one (**1**) and (−)-(2S,3S)-octane-2,3-diol (**2**) in a ratio of 20:80 to 5:95.[12]

Table I. Microbiological Reduction of Octane-2,3-dione (3) by Bakers' Yeast

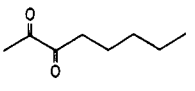
reduced compd	conversn yield,[a] %	absolute confign	$[\alpha]^{25}_J$, deg	ee, %
 **1**	71	2S	+61	92
 **4**	22			
 **5**	7	2S,3R	+19	99

[a] After 1 h of incubation time, as shown by GC analysis.


1


2

A number of methods have been reported for the synthesis of these two compounds, leading to either racemic[13] or chiral molecules.[14] Optically active α-ketol **1** and diol **2** have been obtained by Mori et al.[14b] by chemical methods from 1-octen-3-ol after seven and six steps, respectively. Our chemoenzymatic synthetic route, the microbiological reduction of octane-2,3-dione (**3**), is much shorter, and the starting α-diketone is easily obtained from 2-octanone by hydrolysis of the corresponding oxime.[15]


3

Hydroxy ketone **1**, the minor component of the pheromone, is formed in all cases but rapidly transformed into

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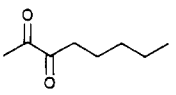
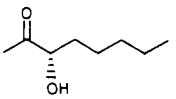
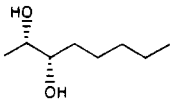
(15) (a) Ferris, A. F. *J. Org. Chem.* **1959**, *24*, 1726. (b) Hartman, W. W.; Roll, L. B. *Organic Syntheses*; J. Wiley: London, 1955; Collect. Vol. III, p 20.

0022-3263/89/1954-3221$01.50/0

Table II. Microbiological Reduction of Octane-2,3-dione (3) by *B. sulfurescens*

reduced compd	conversn yield, % 1 h	24 h	absolute config	$[\alpha]^{25}_J$, deg	ee, %
 3	13	0			
 4	67	0	3*S*	+92	90
 2	20	100	2*S*,3*S*	−16	99

diol. It was isolated only with *Saccharomyces cerevisiae* used as commercial bakers' yeast under nonfermenting conditions, i.e., in distilled water without any nutrient. After 1 h of incubation, the starting dione **3** completely disappeared and a mixture of (2*S*)-2-hydroxyoctan-3-one (**1**), isomeric ketol (3*S*)-3-hydroxyoctan-2-one (**4**), and (2*S*,3*R*)-octane-2,3-diol (**5**) was obtained (Table I). The major product of this mixture was purified on a silica gel column and analyzed. The structure and 2*S* absolute configuration of ketol **1** were determined by comparison of its ^{1}H NMR spectrum and optical rotation with literature data.[13a,14] After chemical conversion into diols, its enantiomeric excess (ee 92%) was determined, as previously described,[1] by GC analysis on a chiral phase, the retention times of diols being compared to those of an authentic sample of (2*S*,3*S*)-octane-2,3-diol.[16] It was not possible to obtain pure **4** with bakers' yeast as its R_f is too close to that of ketol **1** (see Experimental Section).

The reduction of α-dione **3** by bakers' yeast did not afford the major component of the pheromone, diol **2**. With this microorganism, only 2*S*,3*R* diol **5** was isolated (Table I), the structure and absolute configuration of which have been assigned by comparing its physical properties to those in the literature.[13b,17] By GC analysis on a chiral phase it proved to be optically pure (ee 99%).

To obtain pure (2*S*,3*S*)-octane-2,3-diol (**2**), biologically active when mixed with ketol **1**,[12] we selected a fungus, *Beauveria sulfurescens*. After 24 h of incubation, the starting α-diketone had been totally transformed into this diol. After purification, its structure and absolute configuration were determined by comparison with literature data.[14] Its GC analysis on a chiral phase showed **2** to be optically pure (ee >99%) (Table II).

With *B. sulfurescens*, when the incubation time was 1 h, the reaction was incomplete and a mixture of octane-2,3-dione (**3**), (3*S*)-3-hydroxyoctan-2-one (**4**), and (2*S*,3*S*)-octane-2,3-diol (**2**) was obtained (Table II). Even though isomeric ketol **4** is not biologically active, it has to be mentioned that no optical rotation has hitherto been reported for this compound. It was easily purified from the crude extract by column chromatography. Its structure was determined by comparison of its ^{1}H NMR spectrum with the literature data[18] of the racemic compound. The GC analysis on a chiral phase of its corresponding diols, chemically obtained, was compared to that of an authentic sample of the 2*S*,3*S* diol, and its absolute configuration has been assigned as 3*S*. The enantiomeric excess was also determined (ee 90%). Neither ketol **1** nor other diols were detected in the microbial reduction of **3** by *B. sulfurescens*.

In summary, the above synthesis provides a more convenient synthetic route to the components of the pheromone of *X. pyrrhoderus* than previously reported chemical methods. According to the choice of microorganism, either of the two components can be obtained in good yields and high optical purity. The bioconversion conditions had to be carefully studied, especially to obtain the minor component of the pheromone, ketol **1**. Because of its high reactivity, it is rapidly transformed into diol. For example, when bakers' yeast was used as usual, under fermenting conditions, we could not detect this compound in the reaction mixture.

We are currently investigating the scope and limitations of microbiological reductions of various α-diketones to obtain all possible isomers and stereoisomers of ketol and diol products.

Experimental Section

Analytical gas chromatographies were performed on a capillary column filled with 20% Carbowax (20 m × 0.32 mm). The carrier gas was helium at 1.2 kg/cm^2. Oven temperature was 90–150 °C (4 deg/min). Retention times of the products were compared to those of racemic samples obtained by chemical methods. Enantiomeric excesses were determined by GC chromatography using a 26 m × 0.22 mm capillary column packed with Chirasil-L-valine. Thin-layer chromatographies were performed on Schleicher and Schuell F 1500/LS with pentane/ether, 80/20 or 50/50, as eluent I and II, respectively. Column chromatographies were performed on Amicon silica gel (70–200 mesh) with the same eluent as for TLC. Purification of each compound was achieved by bulb-to-bulb distillation. Optical rotations were determined for the mercury J line (λ = 578 nm) at 25 °C. NMR spectra were recorded in $CDCl_3$ solution at 60 or 300 MHz. No elemental analyses were performed. The products obtained being already described, analysis of retention times, NMR spectra, and optical rotation values were considered as sufficient for identification.

Octane-2,3-dione (3). 3-Oximido-2-octanone was obtained from 2-octanone and methyl nitrite in methanol according to Ferris.[15a] Hydrolysis of the oxime and steam distillation were performed according to Hartman et al.[15b] After distillation, octane-2,3-dione was obtained in a yield of 45% from 2-octanone: bp 76–78 °C (12 mm); ^{1}H NMR (60 MHz) δ 0.9 (t, *J* = 6 Hz, 3 H), 1.15–1.60 (m, 6 H), 2.15 (s, 3 H), 2.7–2.9 (m, 2 H).

Reduction of 3 by Bakers' Yeast (*S. cerevisiae*). Two 500-mL conical flasks, each containing 250 mL of water, 10 g of bakers' yeast (Springer brand), and 0.200 g of octane-2,3-dione, were stirred at 200 rpm at 27 °C. After 1 h of incubation, the contents of the flasks were filtered, and the filtrate was extracted continuously with ether overnight. The crude extract was a mixture of 2-hydroxyoctan-3-one (**1**), 3-hydroxyoctan-2-one (**4**), and octane-2,3-diol (**5**), 71%, 22%, and 7%, respectively, as shown by GC analysis. The yield, determined by GC with an internal standard (1-hexen-5-one), was 80%. The residue was purified on a silica gel column with eluent I. 2-Hydroxyoctan-3-one (**1**) was first obtained pure, followed by impure 3-hydroxyoctan-2-one (**4**), and ultimately pure diol **5** was obtained with eluent II.

(+)-(2*S*)-2-Hydroxyoctan-3-one (1): 0.200 g (50% yield); R_f 0.75 (eluent I); GC retention time 14.1 min; ^{1}H NMR (300 MHz) δ 0.90 (t, *J* = 6 Hz, 3 H), 1.2–1.35 (m, 4 H), 1.40 (d, *J* = 7 Hz, 3 H), 1.55–1.70 (m, 2 H), 2.35–2.60 (m, 2 H), 3.6 (s, 1 H exchanged with D_2O), 4.2–4.32 (m, 1 H); $[\alpha]^{25}_J$ = +61° (*c* 0.02, $CHCl_3$) (lit.[14b] $[\alpha]^{20}_D$ = +66.8°); ee 92%.

(+)-(2*S*,3*R*)-Octane-2,3-diol (5): 0.05 g (5% yield); mp 58–60 °C (uncorrected); R_f 0.20 (eluent II); GC retention time 22 min;

(16) We thank Dr. K. Mori (University of Tokyo) for kindly providing biologically active (2*S*,3*S*)-octane-2,3-diol for absolute configuration assignments and enantiomeric excess determinations.

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^{1}H NMR (300 MHz) δ 0.91 (t, J = 6 Hz, 3 H), 1.16 (d, J = 7 Hz, 3 H), 1.20–1.57 (m, 8 H), 1.70 (s, 2 H exchanged with D_2O), 3.60–3.68 (m, 1 H), 3.77–3.88 (m, 1 H); $[\alpha]^{25}_J$ = +19° (c 0.05 $CHCl_3$) (lit.[17] $[\alpha]^{18}_D$ = +22°); ee 99%.

Reduction of 3 by *B. sulfurescens*. *B. sulfurescens* (ATCC 7159) was grown in 500-mL conical flasks containing 100 mL of the following medium: glucose, 30 g/L; peptone, 10 g/L; K_2HSO_4, 1 g/L; $MgSO_4$, 0.5 g/L; KCl, 0.5 g/L; $ZnSO_4$, 0.3 g/L; $FeSO_4 \cdot 7H_2O$, 0.01 g/L in tap water. After 24-h cultivation on a rotary shaker at 27 °C, the mycelium was harvested by filtration, washed four times with saline (8 g/L), and compressed with suction for 10 min. Parts of wet mycelium (5 g) were resuspended in 500-mL conical flasks containing 50 mL of distilled water and 0.050 g of octane-2,3-dione (3). The reaction was carried out at 27 °C with stirring.

A. Twenty-four-Hour Incubation. After 24 h, the contents of 10 flasks were filtered and the filtrate was continuously extracted with ether overnight. The crude extract contained solely (2*S*,3*S*)-octane-2,3-diol (2), which was easily purified by silica gel column chromatography using eluent II. The yield determined with an internal standard (1-hexen-5-one) was 80%.

(−)-(2*S*,3*S*)-Octane-2,3-diol (2): 0.350 g (70%); R_f 0.30 (eluent II); GC retention time 20.9 min; ^{1}H NMR (300 MHz) δ 0.91 (t, J = 6 Hz, 3 H), 1.21 (d, J = 7 Hz, 3 H), 1.20–2.10 (m, 8 H), 1.64, 2 H, exchanged with D_2O), 3.32–3.41 (m, 1 H), 3.56–3.69 (m, 1 H); $[\alpha]^{25}_J$ = −16° (c 0.03, $CHCl_3$) (lit.[14b] $[\alpha]^{20}_D$ = −18.5°); ee 99%.

B. One-Hour Incubation. After 1 h, the crude extract was composed of octane-2,3 dione (3) (13%), (3*S*)-3-hydroxyoctan-2-one (4) (67%), and (2*S*,3*S*)-octane-2,3-diol (2) (20%) as shown by GC analysis. The compounds were purified by silica gel column chromatography using successively eluent I and eluent II, and ketol 4 was obtained pure.

(+)-(3*S*)-3-Hydroxyoctan-2-one (4): 0.200 g (40% yield); R_f 0.70 (eluent I); GC retention time 14.4 min; ^{1}H NMR (300 MHz) δ 0.9 (t, J = 6 Hz, 3 H), 1.20–1.60 (m, 6 H), 1.75–1.90 (m, 2 H), 2.20 (s, 3 H), 3.47 (s, 1 H exchanged with D_2O), 4.15–4.24 (m, 1 H); $[\alpha]^{25}_J$ = +92° (c 0.03, $CHCl_3$); ee 90%.

Acknowledgment. This work was supported by the CNRS within the framework of ATP "Messagers chimiques". We thank Dr. M. F. Renard, G. Kergomard, and M. Sancelme for help in performing parts of the study and Dr. K. Mori (University of Tokyo) for kindly providing biologically active diol.

Registry No. 1, 84435-13-2; 2, 84518-30-9; 3, 585-25-1; 4, 86838-20-2; 5, 66007-44-1; 3-oximido-2-octanone, 584-92-9.

An Unusual Dimer of 2-Mercaptothiophene

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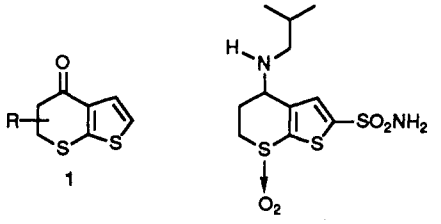
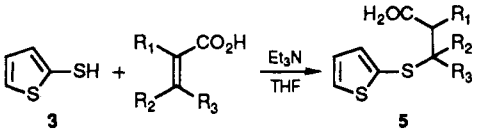
Received January 12, 1989

In previous communications,[1,2] we described the synthesis of various 5,6-dihydro-4*H*-4-oxothieno[2,3-*b*]thiopyrans (1). Recently, interest has increased in the preparation of derivatives of this ring system due to the pharmacology[3] associated with 5,6-dihydro-4*H*-4-[(2-methylpropyl)amino]thieno[2,3-*b*]thiopyran-2-sulfonamide 7,7-dioxide (2) (MK-927) as a carbonic anhydrase inhibitor (CAI) useful in the treatment of glaucoma.[4] Reaction of 2-mercaptothiophene (3) with substituted acrylic acids followed by Friedel–Crafts cyclization provides a facile entry into the synthesis of a large variety of thieno[2,3-*b*]thiopyrans.[2] Since 2-mercaptothiophene[5] is an essential starting material in these synthetic strategies, we report on an unusual dimerization reaction observed for 3.



1 2 (MK-927)

Interestingly, 2-mercaptothiophene (3) slowly solidifies on standing. HPLC analysis[6] of a sample of 3 that was stored in a refrigerator for several months under a blanket of nitrogen indicated that the mixture consisted of approximately 7% 3, 93% of an unidentified compound, and a trace amount of a third component (<0.5%). Conversion of 3 to the disulfide 4 by air oxidation[7] was the most obvious concern. However, reaction of this mixture with acrylic acids, as previously described,[2] gave nearly quantitative yields of 3-(2-mercaptothiopheneyl)-substituted propionic acids 5. This result indicated that the major product was not the disulfide 4. The third component was subsequently identified as the disulfide 4[7] by HPLC comparison with authentic material.



3 5

Trituration of the solid with hexane gave a yellow compound, which by elemental and mass spectral analyses[8] was found to be a dimer of 3. The mass spectrum showed a major fragment at m/z 116, the ion of 3, as well as the parent ion at 232. Additionally, the structural assignment of this dimer was based on NMR analyses. Three aromatic and five aliphatic protons were found in the ^{1}H NMR spectrum.[9] Further inspection of the proton couplings showed that the structure of the dimer must be 6. Results

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(4) Hennekes, R.; Pfeiffer, N.; Lippa, E.; Garus, H.; Grehn, F.; Jaeger, A. *ARVO*, Sarasota, FL, May 1–6, 1988.

(5) Compound 3 was obtained from Trans World Chemicals, Inc., Rockville, MD.

(6) HPLC's were run on a Spectra-Physics 8700XR equipped with a variable wavelength detector set at 210 nm and a Waters C-18 μ-Bondapak column using a flow rate of 3.0 mL/min. The column was run at 35 °C using gradient elution with 95% 0.1% H_3PO_4 and 5% CH_3CN to 5% 0.1% H_3PO_4 and 95% CH_3CN over 30 min. Under these conditions, 3 was eluted in 12.6 min, 6 in 18.9 min, and 4 in 21.2 min.

(7) Challenger, F.; Miller, S. A.; Gibson, G. M. *J. Chem. Soc.* **1948**, 769. In this report the authors also claim that 2-mercaptothiophene (3) is easily oxidized by air to the disulfide and, therefore, stored under nitrogen. In direct contrast, samples of 3 stored in air do not produce large amounts of disulfide 4, but, instead, are converted mainly to dimer 6. The sample of disulfide was not a solid as reported by Challenger; however, 4 was adequately characterized by mass spectral analysis. Noteworthy, the dimer 6 may be considered as a protected form of 3 which is resistant to air oxidation.

(8) Mp 34–36 °C (*n*-BuCl). Anal. Calcd for $C_8H_8S_4$: C, 41.34; H, 3.47. Found: C, 41.13; H, 3.31. The mass spectrum was taken on a VG MMZAB-HB spectrometer at an ionizing energy of 70 eV and the data was processed by a VG 11-250 data acquisition system.

(9) The proton NMR spectrum was obtained at 360 MHz (Nicolet NT-360) in $CDCl_3$. Chemical shifts are referenced to tetramethylsilane. Chemical shift in ppm (splittings in hertz, assignment): 3.01 (17.9, 9.5, H-3a), 3.35 (18.0, 6.2, 0.4, H-3b), 3.97 (9.5, 8.7, 6.1, 6.1, H-4), 3.67 (11.5, 8.7, H-5a), 3.74 (11.5, 6.0, H-5b), 7.23 (3.5, 1.3, H-8), 7.06 (5.4, 3.6, H-9), and 7.47 (5.4, 1.3, H-10).

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