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Highly stereoselective reduction of 4-Aryl-2-oxo but-3-enoic carboxylic esters by plant cell culture of *Daucus carota*☆

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Abstract

A highly enantioselective preparation (92–99% enantiomeric excess, 100% conversion) of various 4-aryl-2-hydroxy but-3-enoic carboxylic acid esters from the corresponding 4-phenyl-2-keto but-3-enoic acid esters mediated by plant cell cultures of *Daucus carota* under mild and environmentally benign conditions in aqueous medium is described.

Keywords: *Daucus carota*; Plant tissue culture; Asymmetric reduction; ∝-Hydroxy β,γ-unsaturated arylidine esters

1. Introduction

Chiral α-hydroxy carboxylic acids and their esters are valuable intermediates in the preparation of many biologically active molecules and methods for their preparation are reported [1–3]. Multifunctional chiral α-hydroxy carboxylic acid esters, e.g. chiral α-hydroxy-but-3-enoic carboxylic acid esters are of special interest [4] since they allow the formation of additional chiral centres, with the C-2 hydroxyl group providing an internal control element for stereoselective transformations of the adjacent alkene e.g., stereoselective epoxidations, such as the Sharpless epoxidation [5], dihydroxylation [6] and aminohydroxylation [7]. To date, few methods have been reported for the synthesis of optically pure α-hydroxy-but-3-enoic carboxylic acid esters. These include both—chemical [8] and biocatalytic [9,10] methods. In procedures which involve resolution of the racemate [10], there is always 50% of the unwanted enantiomer unlike asymmetric reduction which ideally results in the production of only one enantiomer in high optical and chemical yields. The enantioselective reduction of α-keto, β,γ-unsaturated acids, catalysed by lactate dehydrogenase has been reported [9] where the addition of expensive external cofactors (NADH, NADPH) is essential. The use of whole cells obviates this problem and has been reported under stringent anaerobic conditions [11]. Plant cell cultures have been employed for the enantioselective transformation of important foreign synthetic substrates as well as secondary metabolites and have been shown to be good biochemical systems for enantioselective synthesis [12–14]. Of all the plant tissues involved in organic transformations reported so far, carrot seems to be very efficient for asymmetric reduction—both as tissue culture cells [13] and cells from the full grown root [15,16]. We have reported the reduction of the 2-oxo-4-phenyl butanoic acid ethyl ester to the corresponding (*R*)-2-hydroxy-4-phenyl butanoic ethyl ester in >99% ee and 100% conversion by plant cell cultures of *Daucus carota* [17]. In our continued efforts to prepare optically pure α-hydroxy acid esters, we have extended the use of plant cell cultures for other organic transformations. Herein, we report for the first time, asymmetric reduction of 4-aryl-α-oxo-but-3-enoic carboxylic acid esters to 4-aryl-α-hydroxy-but-3-enoic carboxylic acid esters mediated by *D. carota* tissue culture cells (Scheme 1) in high ee and conversion.

2. Results and discussion

Bioreduction of 4-aryl-2-hydroxy but-3-enoic acid esters **1a**–**8a** (as shown in Table 1) by plant tissue culture cells of

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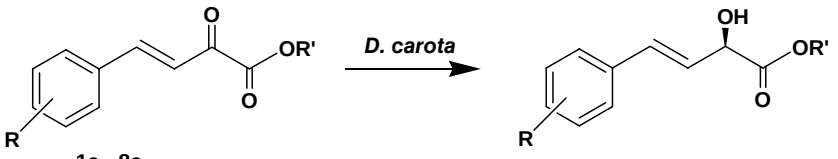

1a - 8a

92 - 99% ee ; 100% conversion

1b - 8b

1. R = H; R' = CH_3
2. R = H; R' = CH_2 CH_3
3. R = *p*-Cl; R' = CH_3
4. R = *p*-Cl; R' = CH_2 CH_3
5. R = *o*-Cl; R' = CH_3
6. R = *o*-Cl; R' = CH_2CH_3
7. R = *p*-CH_3; R' = CH_3
8. R = *p*-CH_3; R' = CH_2CH_3

Scheme 1.

D. carota gave the corresponding hydroxy esters **1b**–**8b** in >92% ee and 100% conversion. Reaction was carried out at 27 °C, 100 rpm for 10 days. The product was isolated using ethyl acetate. The enantiomeric excess of the product hydroxy esters was determined by chiral HPLC. As can be seen in Table 1, the reduction of methyl and ethyl esters of all the compounds studied showed high ee and complete conversion to the reduced product in the presence of plant cell cultures of *D. carota*. The methyl and ethyl esters of, 4-(*p*-methyl)-phenyl-2-hydroxy but-3-enoic acid (**7b** and **8b**) are the only exceptions which are formed in slightly lower ee (92–93%). The nature (electron-withdrawing or electron-donating) and position of the substituent on the aromatic ring viz. *p*-chloro, *o*-chloro and *p*-methyl did not show any marked differences in the optical yields of the reduced products. Sodium borohydride reduction of **1a** gave the unsaturated diol while reduction using palladium/carbon gave the corresponding saturated hydroxy ester [18]. Thus, unlike biocatalytic reduction as reported in this study which selectively reduces the keto group and not C=C, chemical catalysts do not show the distinct selectivity for the reduction of the keto functional group of 4-phenyl-2-keto but-3-enoic ethyl ester. Asymmetric reduction of the unsaturated 2-oxo carboxylic esters (**3a**–**8a**) has not been reported so far. Chemical methods have been reported for asymmetric reduction of esters **1a** and **2a** [8c, d] where as biocatalytic methods have been employed for asymmetric reduction of keto acids of the esters **1a**–**6a** [9,11]. Both (*R*)- and (*S*)-4-phenyl-2-hydroxy but-3-enoic ethyl esters have been prepared by asymmetric acylation of cinnamaldehyde followed by asymmetric dihydroxylation [8b]. 4-Aryl-2-hydroxy but-3-enoic acid methyl ester has also been resolved biocatalytically [10]. But as per exhaustive literature search using Scifinder, there is no report in literature on optically pure substituted 4-aryl-2-hydroxy acid esters (**3b**–**8b**). This is the first report of preparation of these optically pure chiral synthons. Thus, plant cell cultures of *D. carota* catalyze the formation of optically pure 4-aryl-2-hydroxy but-3-enoic acid esters i.e. **1b**–**8b** with excellent enantiomeric excess and in 100% conversion. Isolated yields for ethyl esters (**2b**, **4b**, and **8b**) were higher (67–73%) as compared to the corresponding methyl esters (**1b**, **3b**, and **7b**) which gave a yield of 62–63%. The yield for *o*-chloro substituted methyl and ethyl esters (**5b** and **6b**) was 52–55% (Table 1).The reaction is done in water and no cofactor is added making it an attractive process for the preparation of optically pure 4-aryl-2-hydroxy but-3-enoic acid esters. The optical rotation of the hydroxy

Table 1
Reduction of 4-aryl-2-keto but-3-enoic acid esters by the tissue culture cells of *D. carota*

S. no.	Product		Time (day)	Conversion (%)	ee (%)	[a]Absolute configuration	Yield (%)
	R	R′					
1	H	CH_3	10	100	98	R	62
2	H	CH_2CH_3	10	100	98	R	73
3	*p*-Cl	CH_3	10	100	>99	R	63
4	*p*-Cl	CH_2CH_3	10	100	97	R	67
5	*o*-Cl	CH_3	10	100	96	nd	52
6	*o*-Cl	CH_2CH_3	10	100	98	nd	55
7	*p*-Me	CH_3	10	100	93	nd	62
8	*p*-Me	CH_2CH_3	10	100	92	nd	68

nd: Not determined.

[a] Assignment of absolute configuration was based on reported literature data.

ester **1b** and hydroxy acids obtained by the hydrolysis of the corresponding esters viz., **2b**–**4b** were measured and compared with those reported in the literature [4,11] to assign the absolute configuration, respectively. The ^{1}H and ^{13}C NMR (400 and 100 MHz) of the methyl and ethyl esters of 4-phenyl-2-hydroxy-3-butenoic acid (**1b** and **2b**) obtained were compared with the ^{1}H and ^{13}C NMR (200 and 50 MHz) reported in literature [8b]. ^{1}H and ^{13}C NMR of the hydroxy esters (**3b**–**8b**) are being reported for the first time.

3. Conclusion

We have shown that environmentally benign plant tissue culture cells of *D. carota* in aqueous medium can be used for the highly stereoselective reduction of 4-aryl-2-keto but-3-enoic acid esters to the corresponding hydroxy acid esters in high enantiomeric excess and yield. Since it is possible to alginate cells of *D. carota* and use them in organic transformations [17] this may well be a method of choice for the preparation of these valuable optically pure carboxylic esters.

4. Experimental

Optical rotations were recorded on a Jasco Dip 370 digital polarimeter. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 solutions on JEOL and Bruker 400 MHz spectrometers and chemical shifts were reported in ppm. HPLC analysis was performed on a Jasco PU-1580 liquid chromatograph. The enantiomeric purities (% ee) of **1b**–**8b** were determined by the HPLC analysis in comparison with racemates. The column used was 4.6 mm × 250 mm Chiralcel OD-H (Daicel). The mobile phase was hexane–isopropanol (98:2) at a flow rate of 1 ml min^{-1} and the absorbance was monitored using a UV detector at 254 nm wavelength. All starting materials were prepared according to literature procedure [19].

4.1. General procedure for the reduction of α-oxo, β,γ-unsaturated arylidine esters with plant cell cultures of Daucus carota

4.1.1. Protocol for carrot seed initiation, callus induction and cell suspensions

Seeds of carrot were sterilized by washing in 70% ethanol, followed by 2% sodium hypochlorite and finally with sterile distilled water. The sterilized seeds were then dried on sterile filter paper and incubated in Murashige & Skoog (MS) basal salts medium [20] in petriplates for germination. Hypocotyls (part below the cotyledon) of germinated seedlings of carrot formed were cut into 1 cm pieces and added to the MS basal salts medium amended with 2,4-dichlorophenoxy acetic acid at 2.26 μM (0.5 mg/l) for incubation. Calli (soft, thick mass of cells) (1 g) obtained after incubation was suspended in 50 ml of the same medium in an Erlenmeyer flask (250 ml). Cells were harvested by centrifugation at 3000 rpm for 20 min at room temperature in a Sorvall refrigerated centrifuge (RT6000B, USA) and weighed to determine the biomass. The harvested cells (2 g/flask) were suspended in 50 ml of MS basal salts medium containing the growth regulator benzyl adenine purine (BA; 8.87 μM or 2 mg/l) (D10 medium). At the end of the incubation, the cells were harvested and resuspended in D10 medium. After 14 days of incubation in the dark, test samples of the keto esters (50 mg/50 ml culture) were added, and incubated for 10 days at 100 rpm. Control experiments were done wherein only the solvent (usually ethanol or methanol) was added. The experiments with the keto compounds were done in duplicates. After 10 days the cells were filtered off and the hydroxy product was extracted from the filtrate.

4.2. Determination of conversion and optical purity of the product

The cell free culture filtrate was extracted with ethyl acetate (3 × 10 ml). The organic phase was then dried over anhydrous Na_2SO_4 and concentrated under vacuum. The conversions were determined by HPLC using a Sil-C18 column (size 4.6 mm × 250 mm) by comparing the retention time of the product obtained with that of the keto ester (reactant) and standard hydroxy ester (expected product). The mobile phase used was acetonitrile:water (85:15). The hydroxy products were obtained in 100% conversion. The ee of the hydroxy esters (**1b**–**8b**) was determined by chiral HPLC using Chiralcel OD-H column using hexane: isopropanol (98:2) as the mobile phase. The retention times of the two enantiomers of the racemates (**1b**–**8b**) are as follows: **1b** (26.18 and 34.86 min); **2b** (19.20 and 25.067 min); **3b** (40.43 and 47.85 min); **4b** (25.13 and 28.48 min); **5b** (35.56 and 39.44 min); **6b** (21.65 and 23.94 min); **7b** (41.94 and 46.27 min) and **8b** (27.12 and 29.69 min). The chiral columns used were Chiralcel OD-H and OJ-H for compounds **1b**–**2b** and **3b**–**8b**, respectively. The optical rotation of the hydroxy ester **1b** and hydroxy acids obtained by the hydrolysis of the corresponding esters viz., **2b**–**4b** were measured and compared with those reported in the literature [4,11] to assign the absolute configuration.

4.3. Typical procedure to determine the isolated yield

2-Oxo-4-phenylbut-3-enoic acid ethyl ester (100 mg, 0.490 mmol) in ethanol (0.5 ml) was added to the cell suspension (100 ml) and stirred on an orbital shaker at 100 rpm and 27° C. After 10 days, the cells were harvested and the filtrate was extracted with ethyl acetate, dried over anhydrous Na_2SO_4 and concentrated under vacuum. The resulting solid was purified by column chromatography using hexane:ethyl acetate (98:2). The optically pure product, (*R*)-(*E*)-2-hydroxy-4-phenylbut-3-enoic acid ethyl ester (**2b**) was recovered in 73% overall yield (74 mg, 0.359 mmol)

and characterized by NMR. The ee of this compound was found to be 98%.

4.4. Spectral data for the compounds

1. (*R*)-(*E*)-2-hydroxy-4-phenylbut-3-enoic acid methyl ester (**1b**), pale yellow low melting solid, $[\alpha]_D^{27} = -68.1$ (*c* 1, $CHCl_3$). [lit[4]·$[\alpha]_D = -67.7$ (*c* 0.96 $CHCl_3$)] ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.7(s, 3H), 4.85(d, 1H, $J = 5.6$ Hz), 6.23(dd, 1H, $J_1 = 15.9$ Hz, $J_2 = 5.6$ Hz), 6.8(d,1H, $J = 15.9$ Hz) and 7.2–7.37(m, 5H) ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 52, 71.4, 126, 126.9, 128.2, 128.4, 130, 132.3 and 173. 8.
2. (*R*)-(*E*)-2-hydroxy-4-phenylbut-3-enoic acid ethyl ester (**2b**), white colour solid, $[\alpha]_D^{27} = -90.1$ (*c* 1.92, MeOH) for corresponding acid.[1] [lit[11]·$[\alpha]_D = -90.6$(*c* 1.96 MeOH)] ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.8(dd, 1H, $J_1 = 5.86$ Hz, $J_2 = 1.47$ Hz), 4.3(q, 2H, $J = 7.33$ Hz), 3(bs, 1H), 1.3(t, 3H, $J = 7.33$ Hz), 6.2(dd, 1H, $J_1 = 16.11$ Hz, $J_2 = 5.86$ Hz), 6.7(dd, 1H, $J_1 = 16.11$ Hz, $J_2 = 1.42$ Hz), and 7.2–7.5 (m, 5H), ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 14.3, 62.4, 71.5, 125.7, 126.9, 126.8, 128.7, 132.3, 136.4 and 173.5.
3. (*R*)-*p*-Chloro, (*E*)-2-hydroxy-4-phenylbut-3-enoic acid methyl ester (**3b**), white colour solid, $[\alpha]_D^{27} = -88.2$ (*c* 1.75, MeOH) for corresponding acid[1]. [lit[11]·$[\alpha]_D = -108.8$ (MeOH)] 1H NMR ($CDCl_3$, 400 MHz) δ: 4.8(d, 1H, $J = 5.37$ Hz), 3.8(s, 3H), 3.17(bs, 1H), 6.2(dd, 1H, $J_1 = 5.38$ Hz, $J_2 = 16.11$ Hz), 6.7(d, 1H, $J = 16.11$ Hz) and 7.2(d, 2H, 8.79 Hz) and 7.4(d, 2H, 8.79 Hz), ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 53, 71, 125.8, 127.89, 128.7, 130.99, 133.69, 134.57 and 173.61.
4. (*R*)-*p*-Chloro, (*E)*-2-hydroxy-4-phenylbut-3-enoic acid ethyl ester (**4b**), white colour solid, $[\alpha]_D^{27} = -86.5$ (*c* 1.75 MeOH) for corresponding acid[1]. [lit[11]·$[\alpha]_D = -108.8$ (MeOH)] ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.31(t, 3H, 7.33 Hz), 3.0(bs, 1H), 4.28(q, 2H, 7.33 Hz), 4.87(d, 1H, $J_1 = 1.95$ Hz, $J_2 = 5.37$ Hz), 6.2(dd, 1H, $J_1 = 5.37$ Hz, $J_2 = 16.11$ Hz), 6.7(d, 1H, $J_1 = 1.94$ Hz, $J_2 = 16.11$ Hz), 7.29(d, 2H, 7.81 Hz) and 7.4(d, 2H, 7.81 Hz), ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 14.1, 62.37, 71.1, 126, 127, 128.7, 130, 133, 134 and 173.
5. *o*-Chloro, (*E*)-2-hydroxy-4-phenylbut-3-enoic acid methyl ester (**5b**), colourless liquid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.84(s, 3H), 3.28 (bs, 1H), 4.88(d, 1H, $J = 5.37$ Hz), 6.26(dd, 1H, $J_1 = 5.37$, $J_2 = 16$ Hz), 7.23(d, 1H, 16 Hz) and 7.2–7.4(m, 4H), ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 52.1, 71.28, 127.2, 127.4, 128.3, 128.9, 129.4, 131.2, 132.5, 134.7 and 173.4.
6. *o*-Chloro, (*E*)-2-hydroxy-4-phenylbut-3-enoic acid ethyl ester (**6b**), colourless liquid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.87(d, 1H, $J_1 = 5.37$ Hz), 6.27(dd, 1H, $J_1 = 16$ Hz, $J_2 = 5.37$ Hz), 7.2(d, 1H, 16.1 Hz), 3.2(bs, 1H), 1.3(t, 2H, $J = 7.32$), 4.2(q, 2H, $J = 7.32$ Hz) and 7.2–8.3(m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 14.3, 62.47, 71.58, 127, 127.4, 128, 128.9, 129.1, 129.9, 133.5, 134.6 and 173.2.
7. *p*-Methyl, (*E*)-2-hydroxy-4-phenylbut-3-enoic acid methyl ester (**7b**), white colour low melting solid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.8(d, 1H = 5.37 Hz), 3.7(s, 3H), 2.3(s, 3H), 6.2(dd, 1H, $J_{1=}$5.37 Hz, $J_2 = 15.85$ Hz), 6.7(d, 1H, $J = 15.85$ Hz), 7.1(d, 2H, $J = 7.95$) and 7.2(d, 1H, $J = 7.95$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 14, 52.8, 71.2, 124, 126, 129.2, 131, 132.2, 137.9 and 173.8.
8. *p*-Methyl, (*E*)-2-hydroxy-4-phenylbut-3-enoic acid ethyl ester (**8b**), white colour solid,^{1}H NMR ($CDCl_3$, 400 MHz) δ:4.7(dd, 1H, $J_1 = 5.6$ Hz, $J_2 = 1.07$ Hz), 4.28(q, 2H, $J = 7.32$ Hz), 3.32(s, 3H), 1.2 (t, 3H, $J = 7.32$ Hz), 6.2 (dd, 1H, $J_1 = 5.71$ Hz, $J_2 = 15.8$ Hz), 6.7(dd, 1H, $J_1 = 1.03$, $J_{2=}$15.8 Hz), 7.12 (d, 2H, 7.9 Hz) and 7.26 (dd, 1H, 7.9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 14.1, 21.2, 62.4, 71.6, 124.6, 126.5, 127.2, 132, 133, 137.8 and 173.4.

[1] The absolute configuration of (**2b**–**4b**) esters was assigned by hydrolyzing the esters obtained and specific optical rotations of the corresponding acids were compared with those reported in literature [11].

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