$\mu(Mo_{K\alpha}) = 0.599\ mm^{-1}$, $T = 223(2)$ K. A total of 19166 ($R_{int} = 0.100$) independent reflections were collected up to $2\theta_{max} = 55.00°$. The final $\omega R(F^2)$ for all unique reflections was 0.2162 with a conventional $R(F)$ of 0.08123 for 19166 reflections with $I > 2\sigma(I)$ and 1259 parameters. The molecule crystallizes with two molecules of CH_2Cl_2 and a molecule of H_2O in the lattice. The unit cell contains two unique molecules of the metallaborane, only one of which is shown in Figure 1 without solvent molecules.

3: $C_{25}H_{35}B_{10}P_2RhS$, $M_r = 640.54$, monoclinic, space group $P2_1/n$, $a = 13.2721(1)$, $b = 11.5727(1)$, $c = 19.9181(2)$ Å, $\beta = 94.898\ (1)°$, $V = 3048.13(5)$ Å^3, $\rho_{calcd} = 1.396\ Mg\,m^{-3}$, $Z = 4$, $\mu(Mo_{K\alpha}) = 0.750\ mm^{-1}$, $T = 223(2)$ K. A total of 6964 ($R_{int} = 0.07$) independent reflections were collected up to $2\theta_{max} = 55.00°$. The final $\omega R(F^2)$ for all unique reflections was 0.0597 with a conventional $R(F)$ of 0.0303 for 6943 reflections with $I > 2\sigma(I)$ and 492 parameters.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-103258 and 103259 for **2** and **3**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Insect Desaturases as Unique Analytical Tools To Unravel the Stereochemical Course of the Reduction of Vicinal Ditosylates with Lithium Aluminum Deuteride**

Isabel Navarro, Gemma Fabrias,* and Francisco Camps

The biosynthetic pathways of lepidopteran sex pheromones involve the action of rather unusual desaturases, among which the Δ^{11}-acyl-CoA desaturases are the most common ones.[1] As part of our ongoing studies on the determination of the stereospecificity of fatty acyl desaturases from insects, we have recently demonstrated that in the moth, *Spodoptera littoralis*, formation of (*E*)-11-tetradecenoic acid takes place by stereospecific removal of the *pro*-(*R*) C11-H and the *pro*-(*S*) C12-H from myristic acid.[2] In contrast, desaturation of myristic acid to (*Z*)-11-tetradecenoic acid occurs by stereospecific cleavage of *pro*-(*R*) C11-H and *pro*-(*R*) C12-H, in agreement with the previously reported stereospecificities of the related (*Z*)-11-palmitoyl CoA[3] and (*Z*)-9-stearoyl-CoA desaturases.[4–6]

To continue our investigations, we required an expeditious procedure for the synthesis of *vic*-dideuterated, enantiomerically pure fatty acids.[7] In this context, we thought that asymmetric olefin dihydroxylation followed by tosylation and reduction of the resulting ditosylate with lithium aluminum deuteride might be an appropriate method. However, a recent report on the occurrence of anchimeric effects in the nucleophilic substitution of a *vic*-dimesylate[8] suggested that the stereochemical outcome of the above procedure might be not so straightforward as anticipated. Thus, the evaluation of the stereochemical course of the proposed sythetic pathway was a complex issue, since the determination of the relative stereochemistry of deuterium atoms in the resulting *vic*-dideuterated fatty acids is very cumbersome by current analytical methods.

To solve this problem, we applied the above synthetic procedure to the preparation of a *vic*-dideuterated fatty acid suitable as substrate for a desaturase of known stereospecificity so that the result of the enzymatic reaction would reveal the relative configuration of the vicinal deuterium atoms in the probe. Since the stereochemical courses of both (*Z*)- and (*E*)-11 desaturations of myristic acid in *S. littoralis* is known,[2] the mass of the most abundant isotopomer of both (*Z*)- and (*E*)-11-tetradecenoic acids formed in pheromone glands of insects incubated with both the racemic mixtures of the diastereomers of [11,12,13,13,14,14,14-$^2H_7$]myristic acid

[*] Dr. G. Fabrias, Dr. I. Navarro, Prof. Dr. F. Camps
Department of Biological Organic Chemistry (CID-CSIC)
Jordi Girona 18-26, E-08034-Barcelona (Spain)
Fax: (+349) 3-2045904
E-mail: gfdqob@cid.csic.es

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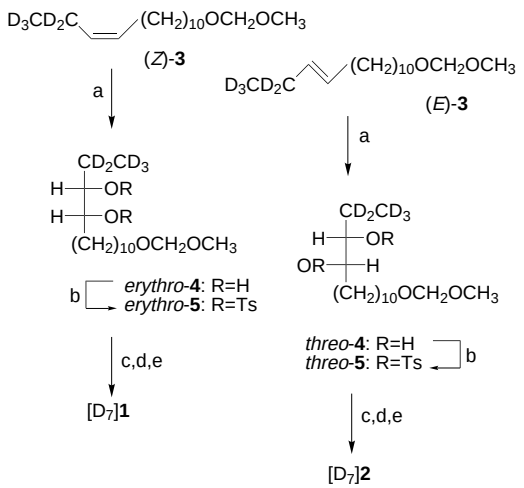
([D$_7$]**1** and [D$_7$]**2**) would reveal the relative configuration of the deterium atoms at C11 and C12 in both tracers.

According to Scheme 1, racemic [D$_7$]**1** and [D$_7$]**2** were obtained by dihydroxylation of (*Z*)- and (*E*)-**3** catalyzed by OsO_4 in the presence of *N*-methylmorpholine *N*-oxide,[9] followed by tosylation of the formed *erythro*- and *threo*-**4**



Scheme 1. a) *N*-methylmorpholine *N*-oxide, OsO_4, *t*BuOH, acetone (*erythro*-**4**, 71%; *threo*-**4**, 65%); b) TsCl, pyridine, then column chromatography (*erythro*-**5**, 23%; *threo*-**5**, 22%); c) $LiAlD_4$, Et_2O, reflux; d) HCl, MeOH; e) CrO_3, H_2SO_4, H_2O ([D$_7$]**1**, 50% from *erythro*-**5**, [D$_7$]**2**, 37% from *threo*-**5**).

diols, respectively, with tosyl chloride and pyridine.[10] Reduction of *eryhtro*- and *threo*-**5** tosylates with lithium aluminum deuteride,[11] followed by deprotection and oxidation afforded the expected probes [D$_7$]**1** and [D$_7$]**2**, respectively, in 5–8% overall yields. These probes were then administered to the pheromone glands as dimethyl sulfoxide solutions (0.1 μL, 10 mg mL^{-1}). Fatty acid methyl esters were obtained by base-catalyzed methanolysis of pheromone gland lipidic extracts, and analyses were performed by GC-MS as previously reported[12] by using a SGE BP-20 capillary column (30 m × 0.20 mm) programmed from 60 °C to 150 °C at 2 °C min^{-1} and then to 260 °C at 7 °C min^{-1} after an initial delay of 2 min. The selected ion-monitoring mode of the corresponding molecular ions for the possible isotopomers was used.

The results of the deuterium-labeling experiments are depicted in Figure 1. In these experiments, the most abundant isotopomer of (*Z*)-11-tetradecenoic acid formed from [D$_7$]**1** was that with six deuterium atoms (*m*/*z* 246, methyl ester). In the light of these results, taking into account that the (*Z*)-11 desaturation proceeds with elimination of C11-H and C12-H of the same configuration,[2] we concluded that the relative spatial location of deuterium atoms in [D$_7$]**1** was *threo*. Likewise, the most abundant isotopomer of (*Z*)-11-tetradecenoic acid formed from [D$_7$]**2** was that with seven deuterium atoms (*m*/*z* 247, methyl ester). A molecular ion was also detected at *m*/*z* 245, corresponding to the compound with five deuterium atoms arising from the loss of two deuterium atoms from the probe; however, its abundance was lower than that of the ion at *m*/*z* 247 because of a primary isotope effect.[13] These data indicated that C11-D and C12-D in [D$_7$]**2** adopt an

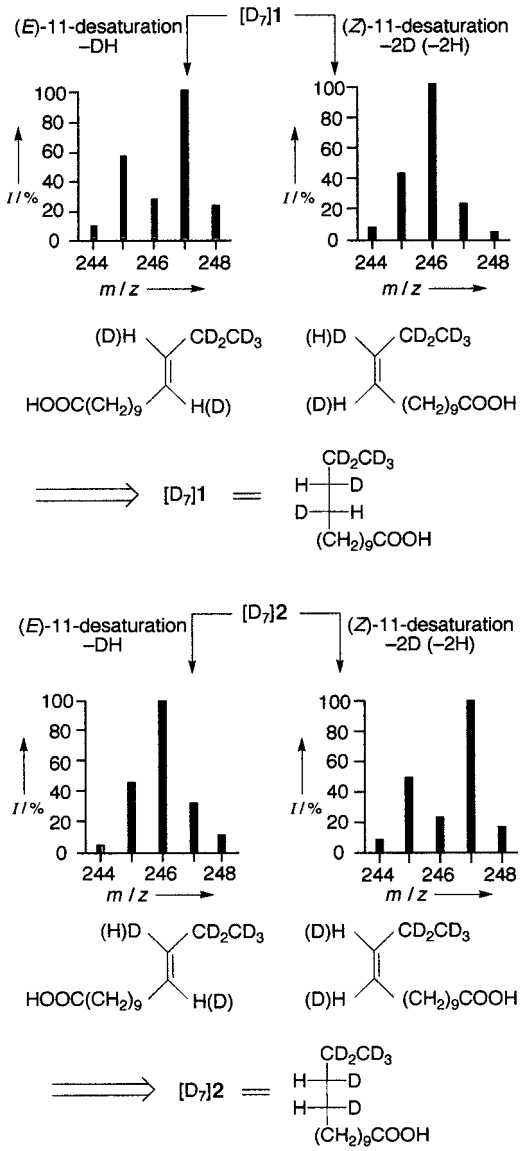


Figure 1. Relative intensities of isotopomers of (*Z*)- and (*E*)-11-tetradecenoic acids, analyzed as methyl esters, formed in pheromone glands incubated with [D$_7$]**1** and [D$_7$]**2**. Percentages correspond to the average mol% of three or four independent experiments performed with groups of five glands. Standard deviations were less than 5% of the mean values in all cases.

erythro configuration. In agreement with these results and with the stereospecificity reported for the formation of (*E*)-11-tetradecenoic acid,[2] the main isotopomer of this acid formed from the probe [D$_7$]**1** was that with seven deuterium atoms, whereas the compound with six deuterium atoms was mainly formed from probe [D$_7$]**2**. Therefore, these results clearly showed that a configurational change occurred during the reduction step of Scheme 1. The possibility that this change occurred at either the dihydroxylation or the tosylation reactions is highly unlikely, since both catalytic olefin dihydroxylation with OsO_4 and formation of tosyl esters are well established reactions.

As exemplified for *erythro*-**5** ditosylate (Scheme 2), a plausible explanation for the observed unexpected result would involve the S_N2 substitution of one tosylate group by a deuteride ion with concomitant displacement of the vicinal

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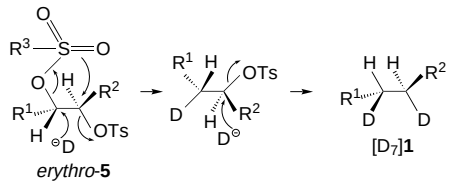

Scheme 2.

tosylate group by the leaving tosyl ester group, thus causing an inversion of configuration at this site. A second inversion at this C atom would then occur by substitution of the remaining tosyl group by a further deuteride ion. The extent of the reduction also occurring through the a priori expected mechanism has not been quantified, but the fact that the proportion of isotopomers of both methyl (*Z*)- and (*E*)-11-tetradecenoate formed from both [D_7]**1** and [D_7]**2** are similar to those formed from the same probes obtained by direct deuteration of the olefins[2] indicates that the unexpected mechanism largely predominated over the expected one. As mentioned above, a similar reaction has been reported by Lin and Shi[8] in the nucleophilic substitution of a 1,2-dimesylate (mesylate = methanesulfonate) with a tosylamine. However, the occurrence of this anchimeric effect is not apparently general. For instance, a cyclic vicinal dimesylate reacts with sodium azide to give the corresponding vicinal diazido derivative arising from single S_N2 displacements at both carbon atoms.[14] Likewise, ditosylates *erythro*- and *threo*-**5** (Scheme 1) react with CsF in polyethyleneglycol to give the corresponding *erythro*- and *threo*-difluorides, respectively.[15]

In summary, we have demonstrated the usefulness of enzymatic reactions as analytical tools to evidence configurational changes not detectable by current analytical techniques. Finally, our results prove that care must be taken when introducing deuterium labeling by reduction of *vic*-ditosylates (and probably other related sulfonate esters) with lithium aluminum deuteride if the configuration of the final products is important.

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Insertion of O_2 into a Chromium – Phenyl Bond: Mechanism of Formation of the Paramagnetic d^2 Oxo Complex [$Tp^{tBu,Me}Cr^{IV}(O)OPh$]**

Alexandra Hess, Markus R. Hörz, Louise M. Liable-Sands, Danielle C. Lindner, Arnold L. Rheingold, and Klaus H. Theopold*

The oxidative functionalization of organic molecules utilizing dioxygen as a reagent remains one of the major challenges for research in catalysis.[1] The ready availability of O_2 and the absence of environmentally harmful by-products are among the attractive features of such processes. Fundamental studies of the role of transition metals in catalytic oxidation must naturally include investigations of the reaction pathways of organometallic molecules with O_2. In this context, the insertion of O_2 into metal – carbon bonds is a reaction of central importance. Despite its significance, only relatively few mechanistic studies of this transformation are available.[2] Herein we report an investigation of the reaction of O_2 with a tris(pyrazolyl)borate chromium phenyl complex, which ultimately yields a phenoxide.

Exposure of a cold (−45 °C) solution in pentane of [$Tp^{tBu,Me}CrPh$][3] (**1**; $Tp^{tBu,Me}$ = hydrotris(3-*tert*-butyl-5-methylpyrazolyl)borate) to an excess of O_2 led to a rapid color change from blue to red. Upon warming to ambient temperature the color of the solution changed again, from red to brown, and workup of the reaction mixture provided the complex [$Tp^{tBu,Me}Cr(O)OPh$] (**2**), which could be isolated in moderate yield (48 %; see Scheme 1). The molecular structure of **2** has been determined by X-ray diffraction,[4] and the result is shown in Figure 1. Despite the steric hindrance of the $Tp^{tBu,Me}$ ligand, which has earned it the title "tetrahedral enforcer",[5] **2** exhibits a five-coordinate chromium atom in a trigonal-bipyramidal configuration. The apparent product of the incorporation of one equivalent of O_2, **2** exhibits an equatorial oxo ligand and an axial phenoxide moiety, which formally results from the insertion of an oxygen atom into the erstwhile chromium – carbon bond. The oxidation state of chromium in the new complex is +IV (d^2); hence, **2** is chemically related to oxo complexes of the type [(porphyrinato)$Cr^{IV}(O)$].[6] However, in contrast to the latter and as indicated by its isotropically shifted and broadened ^{1}H NMR resonances, **2** is paramagnetic, and its effective magnetic moment in the solid state (μ_{eff}(293 K) = 2.6(1) μ_B) is consistent with two unpaired electrons. Paramagnetism of a d^2 mono-oxo complex is rather unusual.[7] We suggest that both frontier orbitals (i.e., d_{xz} and d_{yz}; the *z* axis is along N(3)-Cr-O(2)) are

[*] Prof. Dr. K. H. Theopold, A. Hess, M. R. Hörz, L. M. Liable-Sands, Dr. D. C. Lindner, Prof. Dr. A. L. Rheingold
Department of Chemistry and Biochemistry
Center for Catalytic Science and Technology
University of Delaware
Newark, DE 19716 (USA)
Fax: (+1) 302-831-6335
E-mail: theopold@udel.edu

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