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Heterogeneous asymmetric reactions Part 21. Amino acid derived modifiers in the enantioselective hydrogenation of ethyl pyruvate over supported platinum catalyst☆

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Abstract

New modifiers were prepared from L-tryptophane and tested in the enantioselective hydrogenation of ethyl pyruvate over commercial alumina supported platinum catalyst. Most of these molecules induced only low enantiomeric excesses (ee). (*S*)-3-(1-methyl-indol-3-yl)-2-methylamino-propan-1-ol was found to be the most effective. Using this modifier under mild reaction conditions (1 bar hydrogen pressure, 273 K), enantiomeric excess up to 43% was obtained. Due to the transformation of the modifier evidenced by ESI-MS, a slight increase in hydrogen pressure led to a dramatic drop of enantioselectivity. An interesting inversion of the sense of enantioselectivity was observed in the case of this modifier when the reaction was carried out in acetic acid instead of toluene. A possible explanation for this phenomenon is proposed.

Keywords: L-Tryptophane; Enantioselective; Hydrogenation; Platinum catalyst; α-Keto esters

1. Introduction

The preparation of optically pure products has become a basic requirement in the synthesis of fine chemicals containing chiral centers, especially in the case of compounds used as building blocks in the production of pharmaceuticals, agrochemicals, flavours and fragrances. Many catalysts (metal complexes bearing chiral ligands) are available which exhibit very high levels of enantioselectivity [1–3]. Due to the multiple advantages of heterogeneous catalytic systems such as ease of handling, separation and, most importantly, reuse of the catalyst, extensive efforts have been made for their application in asymmetric synthesis [4]. However, only very few efficiently applicable heterogeneous catalytic systems have been found and these are highly substrate specific. Among the most important ones are two highly enantioselective heterogeneous metal catalyzed hydrogenations, i.e. the tartaric acid modified Raney nickel catalyzed hydrogenation of β-keto esters and β-diketones [5,6] and the cinchona alkaloid modified platinum catalyzed hydrogenation of α-keto esters (Fig. 1). Since its discovery by Orito et al. [7,8], the latter reaction has been studied in detail by several

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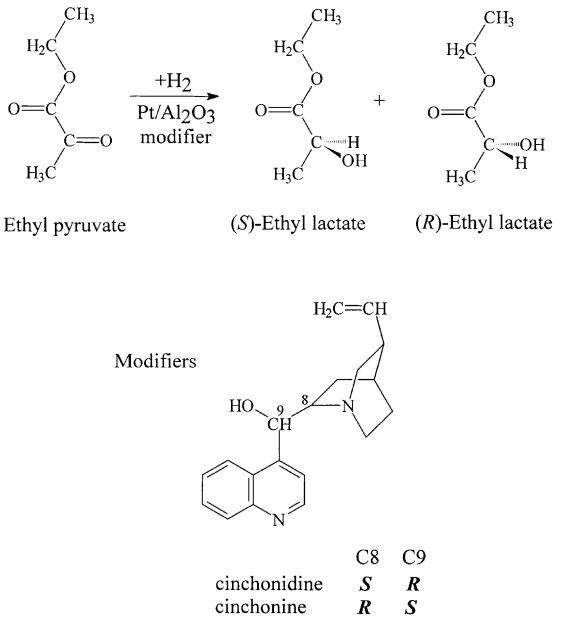

Fig. 1. Heterogeneous enantioselective catalytic hydrogenation of ethyl pyruvate over Pt/Al_2O_3 modified by cinchona alkaloid.

research groups (the results of these studies have been reviewed recently [9–11]). These investigations have been carried out with the aim of understanding how this catalytic system works, nursing the hope of extending its applicability to other types of compounds.

The thorough kinetic investigation of this reaction revealed a very important characteristic, i.e. the high rate enhancement which can be obtained in the presence of the alkaloid modifier. The most likely explanation for this phenomenon is that the half-hydrogenated intermedier is stabilized by the alkaloid molecule, leading to a much higher concentration of these species on the surface and correspondingly to higher reaction rates [10–12].

It is generally accepted that there are three main parts of the cinchona alkaloid molecules, the concerted action of which leads to the high enantioselectivities. The aromatic quinoline moiety serves as an anchoring part on the metal surface, the N atom of the quinuclidine moiety protonated by the solvent has the role of binding the substrate through its carbonyl group and the stereogenic center formed by the C8–C9 chiral atoms induces enantioselection (see Fig. 1). These conclusions were drawn after thorough investigations of the structure–activity and structure–enantioselectivity relationships [13–20] and served as a basis for the development of synthetic, structurally simpler substitutes of the cinchona alkaloids.

Several examples of relatively simple synthetic modifiers yielding enantiomeric excesses (ee) comparable with those obtained with natural cinchona alkaloids were reported [21–27]. Surprisingly, these efforts to find new modifiers for heterogeneous enantioselective hydrogenation were not extended to α-amino acids and their derivatives especially amino alcohols which may easily be prepared from the naturally occurring amino acids. This class of chiral substances has already proved its usefulness in inducing enantioselectivity in several types of organic reactions [28–32]. The meagre interest in using these compounds as modifiers in the hydrogenation of α-keto esters over supported metal catalysts may be explained by the failure in obtaining significant enantioselectivities in the few attempts published up to now [33].

Here we report the synthesis of several L-tryptophane derivatives and their testing for the first time as modifiers in the enantioselective hydrogenation of ethyl pyruvate. The diversification of this very specific heterogeneous catalytic hydrogenation could shed light on new details of the mechanism of the process. ESI-MS has been applied to study the transformation of these new modifier molecules during the reaction. This method had already proved its usefulness in studying the transformation of cinchona alkaloids during the hydrogenation of ethyl pyruvate [19].

2. Experimental

2.1. Materials

L-Tryptophan (99%) and L-tryptophan methyl ester hydrochloride ((*S*)-H-Trp-OMe × HCl) (98%) were purchased from Aldrich and used as received; ethyl pyruvate (Fluka, 98%) was distilled at reduced pressure before use. All other reagents used in the synthesis of the tryptophane derivatives were of analytical grade and used without further purification. Solvents of minimum purity of 99.5% were purchased from Aldrich and Fluka. The 5% Pt/Al_2O_3 catalyst was a

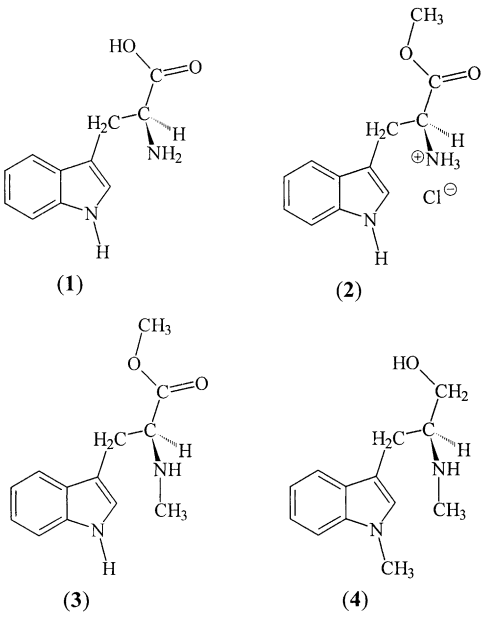

Fig. 2. Molecules synthetized from L-tryptophane and tested in the hydrogenation of ethyl pyruvate.

commercial product (Engelhard 4759) and was pretreated before use for 100 min in 30 cm^3 min^{-1} flowing H_2 at 673 K.

2.2. Preparation of the modifiers

2.2.1. (S)-N-methyltryptophan methyl ester (**3**)

To 0.5 g (*S*)-H-Trp-OMe × HCl (2 mmol) dissolved in 10 cm^3 abs. acetone, 0.55 cm^3 $(C_2H_5)3N$ (4 mmol) and 0.3 cm^3 CH_3I (5 mmol) were added and the mixture was stirred for 30 min at room temperature. The solvent was evaporated to dryness. The crystalline residue was suspended in water, filtered, washed carefully with water and dried. Yield: 0.41 g (77%), mp: 200–202°C, ESI-MS: *m/z* calculated 232, found 233 (MH^+) (Fig. 2).

2.2.2. (S)-3-(1-methyl-indol-3-yl)-2-methylamino-propan-1-ol (**4**)

To 4.46 g H-Trp-OMe × HCl (16 mmol) dissolved in 40 cm^3 dimethylformamide, 4.4 cm^3 $(C_2H_5)3N$ (32 mmol) and 4 cm^3 Boc_2O (17.6 mmol) were added and the mixture was stirred for 2 h at room temperature. The solvent was evaporated in vacuo to dryness and the residue was dissolved in ethyl acetate. The precipitated $(C_2H_5)_3N \times HCl$ was filtered and the filtrate was evaporated in vacuo to give an oily residue which was crystallized from CH_3OH/water. Yield: 5.6 g (82%), mp: 144–146°C. An amount of 3.5 g of this product was dissolved in 30 cm^3 dimethylformamide and to this solution 1.88 cm^3 CH_3I (30 mmol) dissolved in 5 cm^3 dimethylformamide was dripped during 30 min at 40–50°C under stirring in the presence of 7 g Ag_2O (30 mmol). The mixture was stirred for further 24 h at 40–50°C. The resulting mixture was filtered, the filtrate was evaporated in vacuo, the residue was dissolved in ethyl acetate and again filtered to remove the inorganic salts. The organic solution was evaporated in vacuo to dryness to give 2.5 g TLC-pure oily residue which was used without further purification. An amount of 2.5 g of this oil (7.2 mmol) was dissolved in 20 cm^3 CH_3OH and reduced by adding 3 g $NaBH_4$ (182 mmol) in small portions during a period of 30 min. The solution was acidified with 10% $NaHSO_4$ to pH = 2 and then extracted with 50 cm^3 ethyl acetate. The organic solution was washed with water, 10% $NaHCO_3$, water and dried over Na_2SO_4. The solvent was evaporated in vacuo to dryness. The resulted residue was stirred in 10 cm^3 CF_3COOH/CH_2Cl_2 for 1 h at room temperature to remove the Boc-protecting group. After evaporation of the solvent the residue (1 g) was purified by column chromatography on silica gel using CH_2Cl_2/CH_3OH 95:5 as eluent. Yield: 0.6 g (38%) colourless oily product, ESI-MS: *m/z* calculated 218, found 219 (MH^+) (Fig. 2).

2.3. Hydrogenation of ethyl pyruvate

The hydrogenations were carried out (i) in a conventional atmospheric hydrogenation apparatus using a glass reactor equipped with a rubber septum to introduce the reactant via a gas-tight syringe or (ii) in a stainless steel autoclave of 30 cm^3 total volume. In a typical run, 0.05 g of catalyst and 0.005 g of modifier were suspended in 5 cm^3 solvent, the system or the autoclave was flushed with hydrogen and stirred for 1 h at room temperature (25°C). After this pretreatment period 0.25 cm^3 (2.28 mmol) ethyl pyruvate was introduced and the hydrogen consumption recorded. In the case of reaction temperatures other than 25°C the temperature was set to the desired value after

pretreatment, before injecting the substrate into the reactor. After 2 h reaction time the catalyst was filtered and the liquid mixture analyzed.

2.4. Analysis

The analysis was performed using a HP 5890 GC gas chromatograph equipped with a 30 m Lypodex A chiral capillary column and FID. The enantiomeric excesses were calculated according to the equation $ee\% = ([R] - [S]) \times 100/([R] + [S])$. The results were reproducible within ±2%. The reaction products were identified using a HP 5890 GC-HP 5970 MS system equipped with a 60 m DB-1 capillary column. No products other than (*R*) and (*S*)-ethyl lactate were detected by gas chromatography.

Transformation of the modifiers during the reaction was followed by ESI-MS. These measurements were run on a Finnigan TSQ7000 mass spectrometer equipped with a nanospray source, where a gold-coated capillary is used. The high voltage at the capillary was set at 1100 V. The mass range of Q3 was set at 10–1500 u with scan time of 1.5 s. The mass spectrometer and ESI parameters were optimized to give molecular adduct ions (MH^+) in the highest possible abundance.

3. Results

The L-tryptophane derivatives synthetized (Fig. 2) have been used as modifiers in the hydrogenation of ethyl pyruvate under atmospheric hydrogen pressure in three solvents: acetic acid, ethanol and toluene. The results of these experiments are collected in Table 1. For comparison, data obtained in acetic acid without

Table 1
Hydrogenation of ethyl pyruvate under 1 bar hydrogen pressure[a]

Modifier[b]	Solvent[c]	Initial rate[d]	Conversion	Enantiomeric excess	
		($mol\,g^{-1}\,h^{-1}$)	(%)	%	Configuration
–	AcOH	0.021	58[e]	–	
CD[f]	AcOH	0.128	100[g]	90	(*R*)
1	EtOH	0.010	35	3	(*R*)
	AcOH	0.055	99	2	(*R*)
	Toluene	0.100	100	–	
2	EtOH	0.040	61	2	(*R*)
	AcOH	0.024	80	3	(*R*)
	Toluene	0.078	100	10	(*R*)
3	EtOH	0.012	30	2	(*S*)
	AcOH	No reaction occurred			
	Toluene	0.080	86	–	
4	EtOH	0.038	81	15	(*R*)
	AcOH	0.051	100	9	(*S*)
	Toluene	0.078	100	37	(*R*)
		0.023	81[h]	43	(*R*)
		0.088	99[i]	20	(*R*)

[a] Reaction conditions: 0.05 g catalyst, 0.005 g modifier, 5 cm^3 solvent, reaction temperature 298 K, reaction time 2 h.
[b] For abbreviations see Fig. 2.
[c] Ethyl alcohol (EtOH), acetic acid (AcOH).
[d] Determined from the initial hydrogen uptake.
[e] Reaction time: 1.5 h.
[f] Cinchonidine.
[g] Reaction time: 0.5 h.
[h] Reaction temperature: 273 K.
[i] Reaction temperature: 353 K.

modifier and with cinchonidine as modifier are also presented.

As can be seen, the enantiomeric excesses are in most cases very low. In all cases, both the enantioselectivities and the reaction rates were highly dependent on the solvent used. Moderate enantioselectivities were obtained with the 1,2-amino alcohol **4** as modifier. In this case the nature of the solvent had a determinant effect. It is surprising that, while in ethyl alcohol and toluene (*R*)-ethyl lactate was formed in excess, the use of acetic acid as solvent led to the predominant formation of (*S*)-ethyl lactate. By using these modifiers the highest initial rates were obtained in toluene, in contrast with cinchona alkaloids which provided the highest rates in acetic acid. By using **4** as modifier and decreasing the reaction temperature from 298 to 273 K resulted in a moderate increase in the enantiomeric excess while an increase in temperature to 353 K led to a decrease in this value to 20%.

The rates were calculated from the initial hydrogen consumption during the reactions. The comparison of these values, obtained with these new tryptophane derivatives as modifiers in acetic acid, with the rate of the unmodified reaction showed that the ester derivatives **3** and the salt (hydrochloride) **2** decreased the initial rate while modifiers **1** and **4** increased it by a factor of 2–3. However, none of these molecules induced a rate acceleration comparable with that obtained with cinchonidine. Furthermore the initial rates obtained in toluene were higher than those in acetic acid. It is interesting to note that there was no clear correlation between the rate accelerating effects and the values of the enantiomeric excesses obtained in different solvents. For example, the initial rate using **1** was outstandingly high in toluene whereas no enantioselection was observed in this solvent.

By the use of the amino alcohol **4** and changing the solvent from ethyl alcohol to toluene increased both the initial rate and the enantiomeric excess, relatively high values being obtained in this latter solvent. In acetic acid the initial rate fell between the values obtained in ethyl alcohol and in toluene and, surprisingly, enantioselection changed its direction: the (*S*) product was formed in slight but well reproducible excess. According to our knowledge this is the first example of a heterogeneously catalyzed hydrogenation of α-keto esters over platinum catalyst where the sense of enantioselectivity induced by a modifier could be changed merely by changing the solvent. A similar change in the sense of enantioselectivity caused by solvent and/or substituent was recently reported for the same reaction on supported palladium catalyst modified by cinchona alkaloids [34]. However, it is well known that only very poor enantiomeric excesses can be obtained in this reaction over palladium.

The hydrogenation of ethyl pyruvate was also carried out under higher hydrogen pressures; the results are presented in Table 2.

When hydrogen pressure was increased, only small changes, if any, were observed in the case of the modifiers which gave low enantioselectivities at atmospheric pressure. In the case of modifier **4** the increase in hydrogen pressure resulted in a dramatic drop of the enantiomeric excess. The interesting inversion of the sense of enantioselectivity observed in acetic acid could also be observed at higher pressures.

The transformation of the modifiers during the hydrogenations was monitored by mass spectrometry. Using the ESI-MS method made possible the identification of the species formed in the liquid phase or on the catalyst surface and desorbed into the liquid phase. Although the identification of these molecules gave only indirect information about the form in which these modifiers may be adsorbed on the surface, their transformations may provide an explanation for the enantioselectivities and reaction rates obtained. The results of these measurements are listed in Table 3 and the possible structures of the products are illustrated in Fig. 3.

According to these measurements, the transformation of modifier **4** was the least extensive in toluene, especially at 273 K where only minimal transformation was observed. As the temperature was raised, hydrogenation and hydrogenolysis of the modifier occurred, resulting in the formation of an unidentifiable product with *m/z*: 252. This product was probably further transformed by hydrogenolytic cleavages and dimerizations at 353 K leading to a product with *m/z*: 409. This product could also be formed by acylation of the secondary N atom by lactic acid.

In ethyl alcohol the same modifier was transformed mainly to ether **7** and this product was hydrogenated to **8** at low hydrogen pressure. At higher hydrogen pressure (10 bar) the ether was formed in approximatively the same amount as the product with *m/z*: 252 which was also formed in toluene. No hydrogenated ether

Table 2
Hydrogenation of ethyl pyruvate under higher hydrogen pressure[a]

Modifier[b]	Solvent[b]	H_2 pressure (bar)	Conversion (%)	Enantiomeric excess	
				%	Configuration
1	EtOH	10	75	2	(*R*)
3	EtOH	10	95	1	(*R*)
	AcOH	10[c]	No reaction occurred		
		50[c]	No reaction occurred		
4	EtOH	10	97	13	(*R*)
		30	98	9	(*R*)
	AcOH	10	100	4	(*S*)
		30	100	4	(*S*)
	Toluene	2[d]	100	23	(*R*)
		5	100	21	(*R*)
		10	100	19	(*R*)
		30	100	2	(*R*)
		50	100	2	(*R*)

[a] Reaction conditions: 0.05 g catalyst, 0.005 g modifier, 5 cm^3 solvent, reaction temperature 298 K, reaction time 1 h.
[b] For abbreviations see Table 1.
[c] Reaction time: 3 h.
[d] Reaction time: 2 h.

8 could be detected, probably due to extensive hydrogenolysis. In contrast with the reactions carried out in these two solvents in which, in all cases, the initial modifier molecule had the highest relative abundance, in acetic acid only small amounts of the modifier molecule remained unreacted. Two main directions of transformation could be identified in this solvent. At atmospheric hydrogen pressure saturation of the aromatic indolyl system to **5** and subsequent acetylation of the molecule at the secondary N atom to **9** were observed. Under this low hydrogen pressure the acetylated product was predominant whereas at 10 bar pressure the saturated product **5** was more abundant and a product formed by hydrogenolysis **6** also appeared.

These results showed unambiguously that the modifiers underwent more or less extensive transformations during the hydrogenation of ethyl pyruvate. It should be pointed out that pretreatment times and temperatures were identical in all cases, therefore the differences occurring in the transformation of the modifier **4** in toluene at different temperatures were due to its transformations during the reactions.

Table 3
ESI-MS identification of the products formed from **4** during hydrogenation of ethyl pyruvate

Reaction conditions[a]		Relative abundance (%)			
	m/z[b]	219 (**4**)	247 (**7**)	249 (**8**)	252
EtOH	(1)	100	65	30	30
EtOH	(10)	100	20		20
	m/z[b]	219 (**4**)	227 (**5**)	229 (**6**)	269 (**9**)
AcOH	(1)	5	30		100
AcOH	(10)	5	100	30	20
	m/z[b]	219 (**4**)	252	409	
Toluene	(1)	100	25		
Toluene	(1)[c]	100			
Toluene	(1)[d]	100	20	40	
Toluene	(10)	100	30		

[a] For reaction conditions and abbreviations see Tables 1 and 2; hydrogen pressures in parenthesis.
[b] For possible structures see Fig. 3.
[c] Reaction temperature: 273 K.
[d] Reaction temperature: 353 K.

4. Discussion

Several of the tested modifiers induced only very low enantiomeric excesses; however, the synthetized amino alcohol proved to worth more attention. (*S*)-3-(1-methyl-indol-3-yl)-2-methylamino-propan-1-ol (**4**) possesses the structural parts necessary for inducing enantioselectivity. The aromatic indolyl

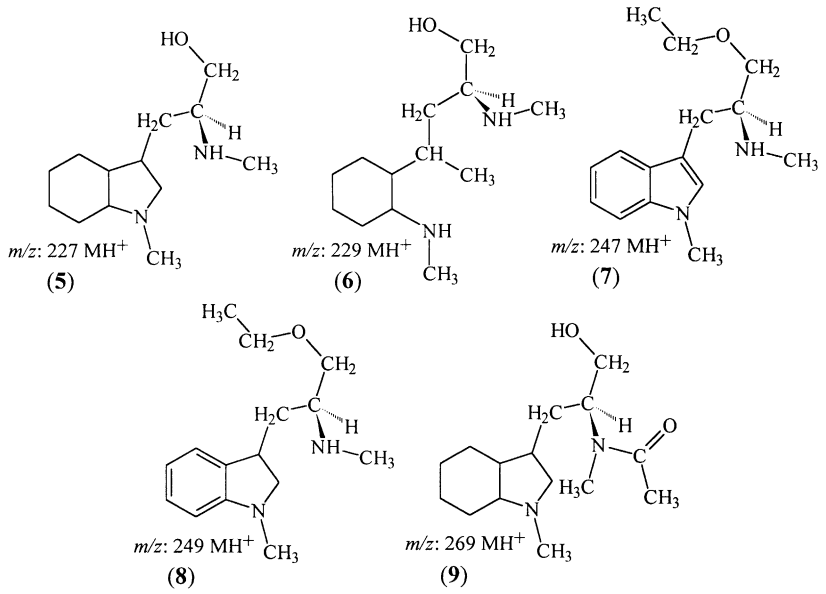

Fig. 3. Major products formed from **4** during the hydrogenation of ethyl pyruvate.

system is capable of anchoring the molecule to the platinum surface, the secondary amine group can provide the site for binding the substrate and there is a chiral center in the molecule which can induce enantioselection. Let us consider the similarities and differences between cinchonidine and this molecule. The C atom corresponding to C9 is achiral while the one corresponding to C8 has the same configuration (*S*) (Figs. 1 and 2) as in cinchonidine. The amino alcohol has an –OH group; however, this is a primary one and is bonded to a C atom more distant from the aromatic moiety. The molecule also possesses a secondary amino group which is bonded to the chiral C atom, thus it is positioned exactly like the tertiary amino group of the quinuclidine ring system in cinchona alkaloids. The distance between the secondary amino group and the –OH group is identical with the corresponding distance in cinchonidine. Contrary with the other molecules used in this study, molecule **4** has the indolyl N atom methylated, resulting in a tertiary N atom of the anchoring moiety.

The structure of this molecule can help explain the moderate enantiomeric excesses obtained by using this modifier. As was evidenced by the ESI-MS measurements the presence of the methyl group on the indolyl N atom inhibited to some extent the hydrogenation of the aromatic moiety during reactions carried out in toluene. The increase in enantioselectivity obtained by decreasing the reaction temperature pointed to the above conclusion, as in this case no transformation of the modifier occurred. When ethyl alcohol was used as solvent, the corresponding ethyl ether was formed. Hydrogenation and hydrogenolysis in this solvent occurred more readily. These transformations explain the lower enantioselectivity values obtained in this solvent.

The most interesting result, to our knowledge without precedents is that after changing the solvent to acetic acid the presence of the same modifier led to the formation of (*S*)-ethyl lactate in excess compared with the excess of the (*R*) enantiomer obtained in the other two solvents. Considering the transformation of **4** during the reaction in acetic acid, the only reason that could cause this inversion of the sense of the enantioselectivity is that the products formed from this modifier will induce enantioselection. According to the ESI-MS results the aromatic ring system is completely hydrogenated in both major products (in the second product the secondary amino group was acetylated), we deem possible that the new chiral center

formed (indolyl-C3) may be the cause of this inversion of the sense of enantioselectivity. However, we have not enough data to ascertain which of the two hydrogenated products is responsible for this phenomenon.

In the hydrogenation of the indolyl group, diastereomeric selectivity may be induced by the chiral center already present in the molecule, leading to the formation of the new chiral center with one configuration in excess which can be responsible for the inversion of enantioselection. Our proposal is supported by the lower enantioselectivities obtained in this solvent as compared to toluene and by the decrease in enantiomeric excess at higher pressures which both are due to the weakening of the adsorption of the saturated molecule on the platinum surface.

Using cinchona alkaloids as modifiers and increasing the hydrogen pressure increases enantioselectivity: the highest values could be obtained at high (100 bar) pressure [9,10]. In the case of **4,** even a slight increase of the pressure led to a significant drop of the enantiomeric excess. However, this effect had already been noticed in the case of other synthetic molecules used as modifiers [21–27]. The authors considered that the improvement of enantioselectivity at higher pressures is related to the presence of the quinoline ring in the cinchona molecules [22] and, on the other hand, the cause of the drop of the enantiomeric excess is due to the partial hydrogenation of the naphthalene ring [28]. Our results support these conclusions. The indolyl moiety being even more sensitive to hydrogenation than the naphthalene ring, a small increase in pressure can cause dramatic drops of the enantiomeric excesses.

To sum up, (*S*)-3-(1-methyl-indol-3-yl)-2-methylamino-propan-1-ol was found to induce moderate enantioselectivities and we are confident that a thorough optimization of the reaction parameters, i.e. catalyst loading, substrate and modifier concentrations or use of other solvents will lead to even higher enantioselectivities. It is also possible that this molecule may act as more efficient modifier in the hydrogenation of other types of substrates which may fit better to the chiral environment induced by this on the metal surface. It should be stressed that this molecule is the first modifier capable of inducing significant enantioselectivity even when the only chiral center of the molecule is not bonded immediately to the aromatic ring system.

5. Conclusions

New compounds were prepared from L-tryptophane and tested as modifiers in the enantioselective hydrogenation of ethyl pyruvate over Pt/Al_2O_3 catalyst. The use of most of these compounds led to low enantiomeric excesses. (*S*)-3-(1-methyl-indol-3-yl)-2-methylamino-propan-1-ol was found to induce moderate enantioselection (up to 43% ee) in toluene under mild reaction conditions, at atmospheric hydrogen pressure and room temperature or below. Raising the hydrogen pressure had a detrimental effect on the enantioselectivity, explained by the inferior resistance of the indolyl aromatic moiety to hydrogenation as compared with the quinoline system present in cinchona alkaloids. Decrease in and inversion of the sense of enantioselectivity were observed when the solvent was changed from toluene to acetic acid. This was explained by the possible role in inducing enantioselectivity of the new chiral center formed by hydrogenation of the aromatic indolyl moiety of the modifier during the reaction.

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