Synthesis of new chiral amino acid ionic liquids

Guilherme S. Caleffi[1] (PG), Ana Cláudia L. Araújo[2] (IC), Ellen S. S. Cruz[2] (IC), Rodrigo S. C. Borges[1] (IC), Sidney R. Santana[2] (PQ), Dayse N. Moreira[1,2*] (PQ).

[1]Laboratório de Síntese Orgânica Medicinal da Paraíba (LASOM-PB), Departamento de Química, Universidade Federal da Paraíba, Campus I, CEP 58051-900, João Pessoa, PB, Brasil.
[2]Laboratório de Química Verde (LQV), Departamento de Ciências Fundamentais e Sociais, Universidade Federal da Paraíba, Campus II, CEP 58397-000, Areia, PB, Brasil.

Keywords: *ionic liquids, amino acids, green chemistry.*

Introduction

The rapidly growing research interest in ionic liquids (ILs) is undoubtedly stimulated by the development of green chemistry. Commonly used ILs, however, are synthetic chemicals and are therefore not as green as desired. Amino acids and their derivatives are the most abundant natural source of quaternary nitrogen precursors, however they have rarely been directly used to prepare the cations in ILs.[1]

Protic amino acid ionic liquids [AA]X can be easily obtained by one-step protonation reactions without any byproduct or complicated post-processing. In addition, they are low cost and can be produced in significant quantities.[2] Herein we report the synthesis of a series of new chiral ionic liquids based on amino acids and bisulfate anion.

Results and Discussion

The formation of $[AA]HSO_4$ is a simple protonation reaction carried out by mixing an equivalent amount of amino acid (glycine, phenylalanine, tyrosine, serine, metionine, triptophane, lysine and glutamine) and aqueous sulfuric acid solution (Figure 1). the mixture was stirred at 60°C during 16 h. The following step involved the evaporation of the water under vacuum, furnishing the desired products. This reaction was also carried out under ultrasound irradiation, however the product yield was lower than the oil bath, even after 2 h of reaction time. The products were obtained in moderate yields (Table 1).

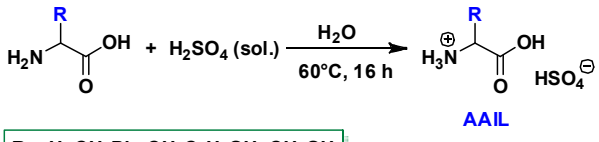

Figure 1. Synthetic route.

Table 1. Product yield.

Amino acid	R	m.p. (°C)	Yield (%)
Phe	CH_2Ph	Oil	76
Tyr	$CH_2C_6H_4OH$	Oil	34
Ser	CH_2OH	Oil	50
Met	$(CH_2)_2SMe$	Oil	75
Trp	CH_2-indol	Oil	66
Lys	$(CH_2)_4NH_2$	120	62
Glu	$CH_2CH_2CO_2H$	110	35

It can be seen from Table 1 that the major products are yellow oils at room temperature. On the other hand, two of them are white solids at room temperature, with melting point higher than 100°C. This result can be related to strong hydrogen bonds involving the additional amino and carboxyl groups.

All compounds were identified by NMR spectroscopy and/or melting point, when appropriate.

Conclusions

The synthetic route applied in the present work was considered environmentally benefic and suitable to obtain a great variety of chiral ionic liquids. In additon, this one-step procedure is an atom-economic reaction without any poisonous by-product. Other studies regarding their catalyst performance in asymmetric synthesis reactions are still in development in our laboratory.

Acknowledgements

The authors acknowledge the financial support of CNPq and UFPB.

[1] G.-h. Tao, L. He, N. Sun, Y. Kou *Chem. Commun.*, **2005**, 3562.
[2] L.-L. Dong, L. He, G.-H. Tao, C. Hu *RSC Advances*, **2013**, *3*, 4806.