Supporting information

Bifunctional quaternary ammonium salts based on benzo[1,2,3]thiadiazole-7-carboxylate as plant systemic acquired resistance inducers

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List of the Contents

General Methods

NMR spectra were obtained in DMSO. Proton chemical shifts are expressed in parts per million (δ scale) Data for 1H and 13C NMR spectra are reported as follows: chemical shift (δ ppm). 1HNMR(300 MHz) and 13CNMR(75 MHz) spectra were recorded on a Varian XL 300 spectrometer at room temperature using *d6*-DMSO as solvent.. The multiplicity of signals is reported as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad (br) or a combination of any of these. Infrared (IR) spectra were recorded on a Bruker Tensor 27. IR data is reported in frequency of absorption (cm^{-1})

Synthesis of deprotonated ASM derivatives

[K][BTHCOO]

In order to obtain the product the reaction between ASM and potassium hydroxide has been performed. To 11,67g ASM 6,22g of potassium hydroxide was added and heated to 110^{o}C in water-toluene system. ASM was dissolved in toluene, inorganic salt and product of hydrolysis moved into water. Side product, volatile methanethiol was also dissolved in water. Reaction was carried out for 12 hours. After the mixture was cooled to room temperature, phases were separated and toluene was washed by water. Water phases were combined and evaporated to the half of the volume. Obtained [BTHCOO][K] was polluted by unreacted potassium hydroxide and because of similar solubilities impossible to separate. Because of this problem solution was acidified by hydrochloric acid to obtain water insoluble BTHCOOH. Obtained product was filtered and washed several times to neutral pH of titrant.

Benzo[1,2,3]thiadiazole-7-carboxylic acid was then reacted with insufficiency of potassium hydroxide to obtain potassium benzo[1,2,3]thiadiazole-7-carboxylate. Reaction was carried out at 100^{o}C overnight and then unreacted BTHCOOH was separated and solvent evaporated. Yield: 90%, mp. 136 ^{o}C,

H^{1} NMR (500 MHz, D_2O) δ/ppm = 8.59 (d, *J* = 7.2 Hz). 8.09 (d, *J* = 6.1 Hz), 7.71 (dd, *J* = 8.1, 7.1 Hz);

C^{13} NMR (500 MHz, D_2O) δ/ppm = 171.59, 157.26, 140.64, 129.89, 129.00, 128.01, 125.73;

IR: ν/cm^{-1} = 3549, 3383, 1609, 1578, 1376, 1284, 1243, 860, 771, 748, 726

Ionic exchanged:

[Chol][BTHCOO]

Solutions of 0,385g of [K][BTHCOO] in 40 ml of MeOH and 0,246g of [Chol][Cl] in 15ml of MeOH was mixed and then solvent was evaporated. Obtained residue was added to acetone and stirred for 12 hours. Undissolved inorganic residue was then separated from solution and then solvent was evaporated. White powder was obtained. Yield: 90%, mp. 122^{o}C

H^{1} NMR (500 MHz, DMSO) δ/ppm = 8.61 (d, *J* = 7.2 Hz), 8.09 (d, *J* = 6.2 Hz), 7.70 (dd, *J* = 8.1, 7.1 Hz), 3.85 (m) , 3.44 (dd, *J* = 5.9, 4.3 Hz), 3.13 (s);

IR: ν/cm^{-1} = 3029, 1598, 1565, 1482, 1463, 1355, 1282, 1062, 787, 772, 736;

[N_{11410}][BTHCOO]
0,2589g [K][BTHCOO] and 0,3824g [N_{11410}][Br] were dissolved in water, and mixed together creating colloid. Mixture was stirred overnight and then chilled to 0^{o}C and centrifuged for 20min at 3000RPM. Oil from bottom was separated and added to dichloromethane. Solution was washed with water and evaporated. Yellow oil was obtained with yield: 50%. mp: 52^{o}C

H^1 NMR (500 MHz, DMSO) δ/ppm = 8.58 (d, *J* = 7.2 Hz); 8.08 (d, *J* = 6.1 Hz); 7.70 (dd, *J* = 8.1, 7.1 Hz); 3.24 (m); 3.00 (s); 1.62 (dt, *J* = 8.2, 5.6 Hz); 1.23 (m); 0.91 (t, *J* = 6.7 Hz); 0.85 (t, *J* = 6.9 Hz);
IR: ν/cm^{-1} = 2924, 2854, 1610, 1578, 1362, 1351, 631, 539

Thermal analyses

Thermal decomposition temperatures were measured using a TGA (TGA Q50 Texas Instrument) under nitrogen atmosphere. Samples were heated from 25^{o}C to 300^{o}C with the heating rate 10 K/min.
Melting point were determined using Different Scanning Calorimetry using STARe System (Mettler Toledo) under argon atmosphere. (flow rate: 10 ml/min). Data was collected using samples between 8-15 mg closed in aluminum pans with heating from 25-160^{o}C and heating rate 10K/min. After initial heating, samples were in constant temperature 160^{o}C for 5 minutes. In the next step samples were cooled from 160^{o}C to -50^{o}C with heating rate 10K/min. Than the samples were in constant temperature -50^{o}C for 5 minutes. The last cycle was heating cycle from -50^{o}C to 160^{o}C with heating rate 10K/min.

Absorbance measurements

Absorbance measurements was performed using spectrophotometer Spectroquant® Pharao 300 Merck in characteristic wavelength for each compounds. A method for measuring the absorbance in a continuous manner was described in the article.
In order to determine the dissolution rate of obtained salts, and compare the results with the dissolution rate for the starting material ASM, the continues dissolution system was assembled that allowed for a constant measurement of absorbance of solution by of UV - Vis method. The test substance with the known weight was placed in a conical flask filled with known amount of water and stirred with magnetic stirrer (250 rpm/min). At the same time, from the top of the flask, continuous flow of solution was taken (using peristaltic pump) and transported through the UV cell. From UV-Vis apparatus outlet solution followed back into the vessel where test substance was dissolved to form a closed, continuous flow system with a capacity of 160ml. The flow rate was set at 8ml/min using a peristaltic pump. The experiment was carried out each time to completely dissolve the test substance. The results of the experiments are presented in the form of a graph of absorbance versus time, where the absorbances of the individual compounds are normalized so that 100% of the absorbance is the absorbance at complete dissolution of the tested substance.

Biological tests

Antiviral tests

In SAR induction test the plants of *N. tabacum* var Xanthi at the stage of three-developed leaves phase were sprayed with 0,1g/l aqueous solutions of ionic liquids and the control was sprayed with distilled water. After six days, treated leaves were infected mechanically with TMV or OLV-1 viruses. As a result of infection local necrotic spots started to appear after few days. Four days following the inoculation a local necrotic spots on the lives treated with IL and from control were counted and compared to each other. Reduction in the number of necrotic spots on the leaves treated with ionic liquid in comparison with the control reflects inhibition of virus infection by induction of plant resistance through the use of ionic liquid. Another manifestation of reducing proliferation of a virus on the plant treated with ionic liquid is the size of spots formed on the leaves.

Antibacterial tests

Antibacterial test was based on the determination of MIC (Minimal Inhibitory Concentration). In each of 90 mm petri dishes bacterial colony was prepared and 4 sterile filter paper discs with a diameter of 5 mm were applied (4 replicates). At each paper disk 5 µl of the test solution was loaded. MIC was determined for both ionic liquids against phytopathogenic bacteria: Pectobacterium carotovorum subsp. carotovorum ATCC 15713 (PCC) and K3 Erwinia amylovora (Eam).