

# Eco-friendly Oxidative Iodination of Various Arenes with a Urea-Hydrogen Peroxide Adduct (UHP) as the Oxidant<sup>1</sup>

Piotr Lulinski, Anna Kryska, Maciej Sosnowski, Lech Skulski\*

Chair and Laboratory of Organic Chemistry, Faculty of Pharmacy, Medical University, 1 Banacha Street, 02-097 Warsaw, Poland  
 Fax +48(22)5720643; E-mail: lskulski@farm.amwaw.edu.pl

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**Abstract:** Three easy eco-friendly laboratory procedures are presented for the oxidative iodination of various activated and deactivated arenes with molecular iodine, in the presence of UHP (percarbamide), a stable, strongly H-bonded, solid urea-hydrogen peroxide adduct as the oxidant.

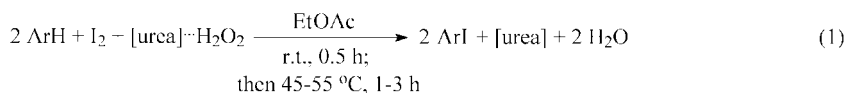
**Key words:** iodoarenes, arenes, halogenation, iodine, peroxides

Aromatic iodides are widely used in organic synthesis; hence many different methods, direct and indirect, or their improvements, have been reported for their effective preparation.<sup>2</sup> Moreover, they are able to form a large variety of stable aromatic hypervalent iodine compounds, which have found increasing applications in modern organic synthesis.<sup>3</sup> Our two latest reviews<sup>4,5</sup> relate and explain a variety of aromatic iodination methods devised in our laboratory, as well as our novel methods of preparing several classes of aromatic hypervalent iodine compounds, easily attainable from aromatic iodides.

Previously, in a series of experimental work (related and explained in Ref.<sup>4a</sup>) we oxidatively iodinated/diiodinated a number of activated and deactivated aromatics (mostly arenes, ArH) with either iodine(I) species I<sup>+</sup>, or iodine(III) species I<sup>3+</sup>, as intermediates, generated from diiodine mostly in anhydrous AcOH/Ac<sub>2</sub>O/conc. H<sub>2</sub>SO<sub>4</sub> (a catalyst and reagent) mixtures. So far we have used the following oxidants for this purpose: pure Pb(OAc)<sub>4</sub> or that prepared in situ from minium (Pb<sub>3</sub>O<sub>4</sub>),<sup>6</sup> CrO<sub>3</sub>,<sup>7</sup> KMnO<sub>4</sub> or activated MnO<sub>2</sub>,<sup>8</sup> NaIO<sub>4</sub> or NaIO<sub>3</sub>,<sup>9</sup> and (diacetoxyiodo)benzene.<sup>10</sup> In the present work we have used a stable solid urea/hydrogen peroxide addition compound (UHP) as the safe and eco-friendly oxidant. The strongly H-bonded<sup>11</sup> UHP (H<sub>2</sub>NCONH<sub>2</sub>···H<sub>2</sub>O<sub>2</sub>), known since 1906,<sup>12</sup> is nowadays commercially available,<sup>13</sup> and its applications in organic and analytical chemistry, as well as in industry, are quickly widening. Likewise as sodium percarbonate and sodium perborate, UHP may be considered as a 'dry carrier'

of the hazardous and unstable hydrogen peroxide, is easy to handle, safe and stable at room temperature. Its ability to release oxidative species in reaction media has made it a useful reagent in organic synthesis.<sup>13</sup> However, nobody has so far used UHP as the oxidant in the oxidative iodination reactions of aromatics, which is the aim of our present work.

At first, we have tried to oxidatively iodinate several aromatic amines, easily oxidizable by most of the oxidants, hence, e.g. primary and secondary aromatic amines were usually oxidatively iodinated as *N*-acyl derivatives.<sup>2</sup> Previously,<sup>9</sup> we succeeded to oxidatively iodinate *N,N*-dimethylaniline (in 65% yield), but for some reason we failed to likewise iodinate *N,N*-diethylaniline and aniline. Chen and co-workers<sup>14</sup> oxidatively iodinated six aromatic amines, within 12 hours at room temperature, with a homogeneous mixture of KMnO<sub>4</sub>/conc. aqueous HI/MeCN, and obtained *para*-substituted products in high yields (71–78%). Quite recently,<sup>15</sup> a new, eco-friendly method for iodination of electron-rich aromatics (some phenols and their *O*-methyl ethers, acetanilide, and three aromatic amines) has been published, with a KI/KIO<sub>3</sub> mixture dissolved in aqueous methanol, and treated with dilute hydrochloric acid. The reactions were run for 2–3 hours under ambient conditions to give the purified products in 65–99% isolated yields. For example, aniline, *N,N*-dimethylaniline, and 4-nitroaniline were monoiodinated in 65, 83, and 96% yields, respectively. Only the iodination of aniline gave a mixture of *para*- and *ortho*-iodoaniline in a ratio of 90:10 as established by GC analysis. In the present work, we have succeeded to oxidatively iodinate seven exemplary aromatic amines (in 41–92% yields) by carrying out the reactions, in the presence of UHP as the oxidant, in neat ethyl acetate (at room temperature for 30 minutes, and then at 45–55 °C for 1–3 hours), but in the absence of conc. H<sub>2</sub>SO<sub>4</sub> (a catalyst). The stoichiometry shown in Scheme 1 is obeyed in our Procedure 1.



Scheme 1

Supposedly, only some transient iodine(I) species,  $I^+$  are acting there as weak electrophiles. The main iodination reactions were completed when the iodine coloration faded. Then, the cooled mixtures were poured into excess aqueous  $Na_2SO_3$  solutions to possibly destroy unreacted diiodine and any oxidizing species. The following simple workups, purification procedures, and final yields of the purified iodinated products are explained in the experimental section, and are listed in Table 1, respectively. To attain the oxidative diiodination of aniline, we used half of the amount added to the starting reaction mixture (with respect to that used for its monoiodination), which resulted in 58% yield of pure 2,4-diiodoaniline.

Recently,<sup>16</sup> we have tried to accelerate the above reactions with microwave irradiation, under an externally attached reflux condenser. We have established that better results are obtained by replacing ethyl acetate with chloroform as the solvent of choice. The microwave assisted oxidative iodination reactions of seven arylamines, with UHP as the oxidant, afforded somewhat lower yields than those presented in Table 1, but the reaction times were shortened to only 10 minutes.

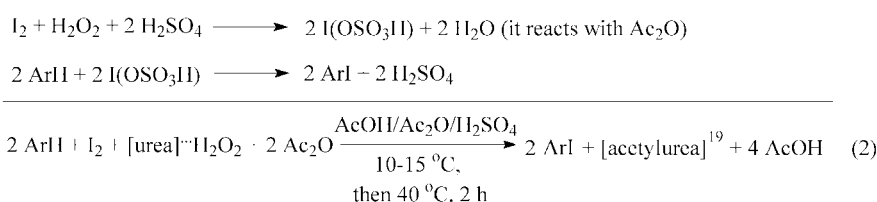
Next, we have devised a possibly optimized method applicable for the oxidative monoiodination of benzene, halobenzenes, acetanilide, uracil, 4-nitrotoluene, 4-nitroanisole, 4-acetylaminobenzoic acid, anisic acid and its methyl ester, as well as for the diiodination of benzene, in the presence of UHP as the oxidant. As previously,<sup>7-10</sup> the oxidative iodination reactions were carried out in anhydrous mixtures of glacial acetic acid with acetic anhydride, with suspended UHP and diiodine, and acidified with varied quantities<sup>17</sup> of conc. (98%)  $H_2SO_4$  added dropwise to the reaction mixtures, while keeping the temperature at 10–15 °C (see experimental). The stoichiometry given in Scheme 2 is obeyed in our Procedure 2.

Some intermediate iodine(I) species  $I^+$ , are supposedly acting as the iodinating agents [in this case,  $I^+$  represents

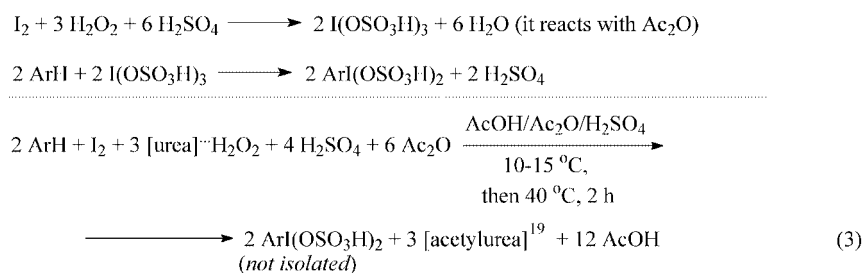
iodine(I) hydrogensulfate].<sup>4</sup> After completing the main iodination reactions, carried out within 2 hours at 40 °C, the strongly acidic final reaction mixtures were poured, after cooling, into excess aqueous  $Na_2SO_3$  solutions. The same simple workups and purification procedures were applied as those in Procedure 1 (see experimental) to give the purified monoiodinated arenes in 22–87% yields (Table 1). When benzene was oxidatively diiodinated, we added half of the amount to the starting reaction mixture (with respect to that used for its monoiodination); the purified 1,4-diiodobenzene was obtained in 54% yield. However, we failed to iodinate anisole, in spite of several attempts.

Benzoic acid and its methyl ester, 4-toluic acid,  $\alpha,\alpha,\alpha$ -trifluorotoluene, 4-nitrotoluene, as well as (for comparison) bromo- and iodobenzene were effectively oxidatively monoiodinated in anhydrous mixtures of glacial acetic acid with acetic anhydride, acidified with varied quantities<sup>17</sup> of conc.  $H_2SO_4$  (see experimental). UHP was applied here in a threefold amount in order to generate more electrophilic iodinating intermediates,  $I^{3+}$  in the anhydrous and strongly acidic iodinating solutions [in this case,  $I^{3+}$  represents iodine(III) hydrogensulfate].<sup>4</sup> The stoichiometry shown in Scheme 3 is obeyed in our Procedure 3.

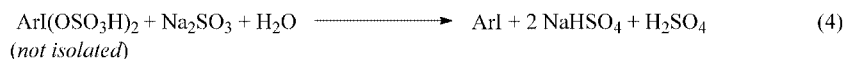
After one suspends UHP, an appropriate arene and powdered diiodine in an anhydrous mixture of glacial acetic acid with acetic anhydride, the conc. (98%)  $H_2SO_4$  should be added very slowly, with stirring and keeping the temperature at 10–15 °C (strongly exothermic reaction). The main iodination reactions were carried out for 2 hours at 40 °C, which resulted in the final reaction mixtures containing the assumed, soluble organic iodine(III) intermediates,  $ArI(OSO_3H)_2$ ,<sup>4</sup> which were poured, after cooling, into excess aqueous  $Na_2SO_3$  solutions to destroy any oxidizing and oxidized species and unreacted diiodine (Scheme 4).



#### Scheme 2



#### Scheme 3



#### Scheme 4

The crude monoiodinated products were isolated and purified similarly to those obtained in Procedures 1 or 2 (see the experimental section) to give pure monoiodoarenes in 18–88% yields. We failed, however to iodinate nitrobenzene, in spite of many attempts. Using Procedure 3, modified as above, we diiodinated benzophenone (46%) and, for comparison, also benzene (44%).

Summing up, our novel easy, relatively inexpensive, and eco-friendly iodinating Procedures 1–3 presented in this paper gave mono- or diiodinated products from some highly activated arylamines, benzene, halobenzenes, and several activated and deactivated arenes in moderate or good yields (Table 1). In our opinion, particularly interesting are our iodination experiments with arylamines and moderately deactivated arenes, except nitrobenzene. It is also of importance that no strongly toxic wastes are left after completing the oxidative iodination reactions reported in this paper (cf. our two former eco-friendly oxidative iodination methods<sup>9,10</sup>).

The structures of the purified iodinated products (their purity and homogeneity were also checked by TLC), all known in the literature, were supported by their melting or boiling points (uncorrected) that were compared with the literature data (Table 1). The structures were supported by elemental analyses (%I), and <sup>1</sup>H NMR solution spectra (not shown here),<sup>20</sup> which were compared with the spectra of authentic samples. Elemental analyses were carried out at the Institute of Organic Chemistry, The Polish Academy of Sciences, Warsaw. <sup>1</sup>H NMR spectra were run at the Department of Chemistry, University of Warsaw. The commercial reagents and solvents used (Aldrich) were purified or dried, if necessary, prior to use. Molecular iodine should be finely powdered in order to facilitate its dissolution in the reaction mixtures.

#### Possibly Optimized Iodinating Procedures

##### General Procedure 1

*Applicable for the Oxidative Iodination of Some Aromatic Amines:* Finely powdered I<sub>2</sub> (0.51 g, 2 mmol; 0% excess) [for the diiodination of aniline, excess I<sub>2</sub> (0.56 g, 2.2 mmol; 10% excess) was added] and 98% UHP (0.25 g, 2.5 mmol; 25% excess) were suspended in neat EtOAc (6 mL). Next, an appropriate arylamine (4.4 mmol; 10% excess) [only 2 mmol (0% excess), when aniline was diiodinated] was added and the obtained mixture was stirred for 0.5 h at r.t., and then at 45–55 °C for 1–3 h, until the iodine coloration faded. After cooling to r.t., the reaction mixture was poured into a stirred solution of Na<sub>2</sub>SO<sub>3</sub> (0.5 g, 3.95 mmol) in H<sub>2</sub>O (70 mL). The precipitate was collected by filtration, washed well with cold H<sub>2</sub>O, air-dried in the dark, and recrystallized from hexane or EtOH (Table 1). The oily or semi-solid crude products, sometimes obtained, were extracted with CHCl<sub>3</sub> (3 × 10 mL), the collected extracts were dried (MgSO<sub>4</sub>) and filtered, the solvent was distilled off, and the solidified residues were recrystallized from hexane or EtOH (Table 1).

##### General Procedure 2

*Applicable for the Oxidative Iodination of Benzene, Halobenzenes and Activated Arenes:* Finely powdered I<sub>2</sub> (0.51 g, 2 mmol; 0% excess) and 98% UHP (0.29 g, 3 mmol; 50% excess) were suspended

in a mixture of AcOH (6 mL) with Ac<sub>2</sub>O (3 mL). Next, an appropriate arene (4.2 mmol; 5% excess) [only 2.1 mmol (5% excess), when benzene was diiodinated] was added. The stirred mixture was cooled to 10 °C, and varied quantities<sup>17</sup> (see below) of concd (98%) H<sub>2</sub>SO<sub>4</sub> were slowly added dropwise, with vigorous stirring, while keeping the temperature at 10–15 °C (exothermic reaction), viz.:

(a) for acetanilide and uracil, 4.00 mL (7.36 g, 75 mmol) of concd H<sub>2</sub>SO<sub>4</sub> was added;

(b) for benzene, bromobenzene, 4-nitroanisole, anisic acid, and its methyl ester, 4.27 mL (7.85 g, 80 mmol) of concd H<sub>2</sub>SO<sub>4</sub> was added;

(c) for chlorobenzene and 4-nitrotoluene, 4.53 mL (8.34 g, 85 mmol) of concd H<sub>2</sub>SO<sub>4</sub> was added;

(d) for 4-acetylaminobenzoic acid, 5.33 mL (9.81 g, 100 mmol) of concd H<sub>2</sub>SO<sub>4</sub> was added; and

(e) for the diiodination of benzene, 6.93 mL (12.75 g, 130 mmol) of concd H<sub>2</sub>SO<sub>4</sub> was added.

The reaction mixture thus obtained was stirred for 2 h at 40 °C, cooled to r.t., and poured with stirring into ice-water (50 g) containing prior dissolved Na<sub>2</sub>SO<sub>3</sub> (0.5 g, 3.95 mmol). The crude iodinated products were isolated, worked up and purified as above in Procedure 1 (Table 1).

##### General Procedure 3

*Applicable for the Oxidative Iodination of Halobenzenes and Deactivated Arenes:* Finely powdered I<sub>2</sub> (0.56 g, 2.2 mmol; 10% excess) and 98% UHP (0.87 g, 9 mmol; 50% excess) were suspended in a mixture of AcOH (8 mL) with Ac<sub>2</sub>O (4 mL). Next, an appropriate arene (4 mmol; 0% excess) [only 2.0 mmol (0% excess), when benzene or benzophenone were diiodinated] was added. The stirred mixture was cooled to 10 °C, and varied quantities<sup>17</sup> (see below) of conc. (98%) H<sub>2</sub>SO<sub>4</sub> were slowly added dropwise, with vigorous stirring, while keeping the temperature at 10–15 °C (exothermic reaction), viz.:

(a) for benzoic acid, 3.20 mL (5.88 g; 60 mmol) of concd H<sub>2</sub>SO<sub>4</sub> was added;

(b) for bromobenzene, iodobenzene, methyl benzoate, and 4-toluic acid, 4.27 mL (7.85 g; 80 mmol) of concd H<sub>2</sub>SO<sub>4</sub> was added;

(c) for 4-nitrotoluene and for the diiodination of benzene, 4.53 mL (8.34 g; 85 mmol) of concd H<sub>2</sub>SO<sub>4</sub> was added;

(d) for the monoiodination of  $\alpha,\alpha,\alpha$ -trifluorotoluene and for the diiodination of benzophenone, 6.40 mL (11.77 g; 120 mmol) of concd H<sub>2</sub>SO<sub>4</sub> was added; and

(e) for nitrobenzene, 12.79 mL (23.54 g; 240 mmol) of concd H<sub>2</sub>SO<sub>4</sub> was added, but the following reaction did not proceed.

The reaction mixture thus obtained was stirred for 2 h at 40 °C, cooled to r.t., and poured with stirring into ice-water (50 g) containing prior dissolved Na<sub>2</sub>SO<sub>3</sub> (2.0 g, 15.8 mmol). The crude iodinated products were isolated, worked up and purified as above in Procedure 1 (Table 1).

*Note:* The yields of the purified iodinated products given in Table 1 were calculated from the total amounts of those reagents (I<sub>2</sub> or arenes), which were used in the reactions in strictly stoichiometric quantities (0% excess).

**Table 1** Iodinated Pure Products Prepared

Substrate	Procedure	Product	Yield (%) <sup>a</sup>	Mp (°C) (S), <sup>b</sup> or bp (°C/mmHg); Lit. <sup>18</sup> mp (°C), or bp (°C/mmHg)
PhNH <sub>2</sub>	1	4-IC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	64	63–65 (H); 63–65
PhNH <sub>2</sub>	1	2,4-I <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NH <sub>2</sub>	58	94–95 (H); 95–96
PhNHMe	1	4-IC <sub>6</sub> H <sub>4</sub> NHMe	41	29–31 (E); 31.5
PhNMe <sub>2</sub>	1	4-IC <sub>6</sub> H <sub>4</sub> NMe <sub>2</sub>	85	81–82 (E); 82
PhNEt <sub>2</sub>	1	4-IC <sub>6</sub> H <sub>4</sub> NEt <sub>2</sub>	60	26–29 (E); 32
2-MeC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	1	4-I,2-MeC <sub>6</sub> H <sub>3</sub> NH <sub>2</sub>	92	86–88 (H); 88, 91–92
4-IC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	1	2,4-I <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NH <sub>2</sub>	80	95–96 (H); 95–96
2-ClC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	1	2-Cl,4-IC <sub>6</sub> H <sub>3</sub> NH <sub>2</sub>	55	70–73 (H); 68, 70–73
PhNHCOMe	2	4-IC <sub>6</sub> H <sub>4</sub> NHCOMe	87	183–185 (E); 184
4-RC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H <sup>c</sup>	2	4-R,3-I-C <sub>6</sub> H <sub>3</sub> CO <sub>2</sub> H <sup>c</sup>	57	222–224 (W); 230
4-MeOC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	2	3-I,4-MeOC <sub>6</sub> H <sub>3</sub> CO <sub>2</sub> H	38	225–228 (M); 233–234
4-MeOC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> Me	2	3-I,4-MeOC <sub>6</sub> H <sub>3</sub> CO <sub>2</sub> Me	42	94–96 (N); 95–97
4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> OMe	2	2-I,4-O <sub>2</sub> NC <sub>6</sub> H <sub>3</sub> OMe	81	96–97 (L); 97
4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Me	2	2-I,4-O <sub>2</sub> NC <sub>6</sub> H <sub>3</sub> Me	72	54–55 (N); 53–54, 61
uracil	2	5-iodouracil	25	273–274 (E); 272 (dec.)
PhH	2	PhI	45	bp 78–80/25; bp 63–64/8
PhH	2	1,4-I <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	54	127–128 (L); 129
PhH	3	1,4-I <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	44	124–126 (L); 129
PhCl	2	4-ClC <sub>6</sub> H <sub>4</sub> I	22	54–55 (E); 57
PhBr	2	4-BrC <sub>6</sub> H <sub>4</sub> I	83	91–92 (L); 91–92
PhBr	3	4-BrC <sub>6</sub> H <sub>4</sub> I	64	89–91 (L); 91–92
PhI	3	1,4-I <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	65	126–128 (L); 129
PhCO <sub>2</sub> H	3	3-IC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	81	187–189 (C); 187–188
PhCO <sub>2</sub> Me	3	3-IC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> Me	84	50–52 (P); 54–55
4-MeC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	3	3-I,4-MeC <sub>6</sub> H <sub>3</sub> CO <sub>2</sub> H	88	208–210 (C); 210–212
4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Me	3	2-I,4-O <sub>2</sub> NC <sub>6</sub> H <sub>3</sub> Me	86	53–55 (N); 53–54, 61
PhCF <sub>3</sub>	3	3-IC <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	18	bp 70–72/38; bp 84–88/60
PhCOPh	3	3-IC <sub>6</sub> H <sub>4</sub> COC <sub>6</sub> H <sub>4</sub> I-3'	46	141–143 (A); 152–153

<sup>a</sup> Yield of pure isolated product. Satisfactory microanalyses obtained for the purified products: I ± 0.3%; their purities and homogeneities were checked by TLC and <sup>1</sup>H NMR solution spectra (not shown here).<sup>20</sup>

<sup>b</sup> S = Solvent used for recrystallization. A: acetone; C: CCl<sub>4</sub>; E: EtOH; H: hexane; L: EtOH–H<sub>2</sub>O (4:1); M: EtOH–H<sub>2</sub>O (2:1); N: EtOH–H<sub>2</sub>O (3:2); P: petroleum ether (bp 35–60 °C); W: H<sub>2</sub>O–EtOH (5:1).

<sup>c</sup> R = 4-MeCONH.

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- (17) Varied quantities of conc.  $H_2SO_4$  added to the reaction mixtures (established by us experimentally and given in the experimental section for each of the arenes iodinated) clearly depended on relative reactivities of the arenes investigated. The more deactivated the arene, the more conc.  $H_2SO_4$  had to be added to catalyze better the oxidative iodination reaction. For more details see either Note 22 in Ref.,<sup>9</sup> or (better) Ref.,<sup>4</sup> pp 1334-1337.
- (18) *Dictionary of Organic Compounds*, 6th ed.; Chapman & Hall: London, **1996**.
- (19) The urea released from UHP is readily acetylated in hot  $Ac_2O/AcOH/concd H_2SO_4$  mixtures to give *N*-acetylurea admixed with *N,N'*-diacetylurea. However, these side products are fully removable from the crude iodinated products during the workup and recrystallization.
- (20) The  $^1H$  NMR solution spectra run in this work to support the structures of the purified iodinated products are presented and discussed in: Lulinski P.; *Ph.D. Thesis* (in Polish); Faculty of Pharmacy, Medical University of Warsaw: Poland, **2002**;