SYNTHESIS OF (2-(PHENYLTHIO)PHENYL)ACETAMIDINES AND RELATED AMIDOXIMES AS POTENTIAL ANTIDEPRESSANTS

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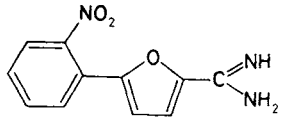
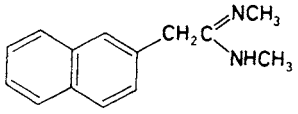
Received July 6th, 1987

Reactions of ethyl (2-(phenylthio)phenyl)acetimidate (*X*) hydrochloride with ammonia and the corresponding amines resulted in amidines *V*—*X*. Heating (2-(phenylthio)phenyl)acetonitrile with 2-aminoethylammonium toluene-4-sulfonate led to the 2-imidazoline *XI*. Reactions of (2-(phenylthio)phenyl)acetonitrile and the lower homologue *XVI* with hydroxylamine gave the amidoximes *XIII* and *XV*; *XIII* was oxidized to the sulfoxide *XIV*. Compounds *VII*, *XI*, and *XIII* showed some antireserpine activity which indicates thymoleptic and antidepressant potentiality. On the other hand, none of the compounds tested did show any noteworthy affinity to the [^{3}H]imipramine and [^{3}H]desipramine binding sites in the rat hypothalamus.

The amidine and the related 2-imidazoline fragment appear rather often in molecules of substances which are described as antidepressants; the experimental agents nitrafudam (*I*) (refs[1,2]). napactadine (*II*) (refs[3–5]), idazoxan (*III*) (refs[6,7]), and fenmetozole (*IV*) (ref.[8]) may be mentioned as examples. The amidoximes as potential antidepressants were the object of one of our previous communications[9]. Within a systematic search after new antidepressants between the basically *ortho*-functionalized diphenyl sulfides[10–12] we are now describing the synthesis and results of pharmacological testing of the title compounds.



I



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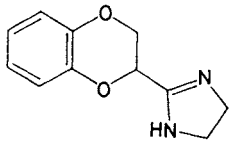

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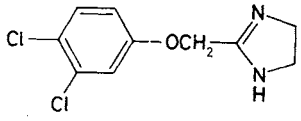
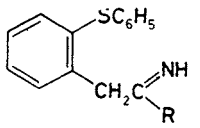


IV

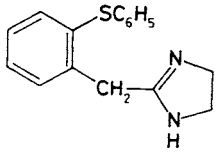
The amidines *V*–*IX* were prepared from (2-(phenylthio)phenyl)acetonitrile[13] by making use of the Pinner synthesis[14]. This nitrile was treated with hydrogen chloride in ethanolic solution which led to the hydrochloride of ethyl (2-(phenylthio)phenyl)-acetimidate (*X*) (cf. ref.[15]). Reaction of *X* hydrochloride with ammonia in ethanol at room temperature and treatment of the crude product with ethanolic potassium hydroxide gave the base *V* which was transformed by neutralization with maleic acid into the 1 : 1 and 2 : 1 maleates. Similar reactions of *X* hydrochloride with piperidine and morpholine in boiling ethanol resulted in hydrochlorides of *VI* and *VII*. Similar reactions with 1-methylpiperazine and 1-(2-hydroxyethyl)piperazine gave oily hydrochlorides which were transformed via crude bases to dimaleates of *VIII* and *IX* (for methods, cf. ref.[16]). The identity of the amidines was confirmed by mass, IR, and ^{1}H NMR spectra.



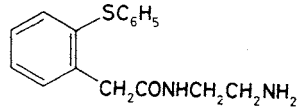
V, R = NH_2 *VI*, R = N⬡ *VII*, R = N⬡O

VIII, R = N⬡NCH$_3$ *IX*, R = N⬡NCH$_2$CH$_2$OH *X*, R = OC_2H_5

For preparing the cyclic analogue of the amidine *V*, i.e. the 2-imidazoline *XI*, method of Oxley and Short[17] was used. (2-(Phenylthio)phenyl)acetonitrile[13] was heated with 2-aminoethylammonium toluene-4-sulfonate to 200°C and the released base was converted to the *XI* oxalate (according to the mass spectrum). Mixture of bases, released from the mother liquors, was chromatographed on aluminium oxide and in addition to some further *XI* a more polar base was obtained which was also converted to the oxalate. Analysis and the mass spectrum indicated the product to be *XII* which was confirmed by the IR spectrum (amide bands at 1 550 and 1 660 cm^{-1}). It is the product of hydrolysis of *XI* formed probably during the isolation procedure. A similar case of hydrolysis of a 2-imidazoline was investigated previously and it was found that it proceeds in alkaline[18] as well as in neutral medium[19].

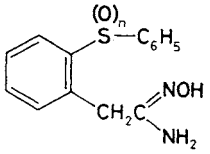


XI

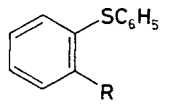


XII

Reaction of (2-(phenylthio)phenyl)acetonitrile[13] with hydroxylamine base in boiling methanol (method[20]) gave the amidoxime *XIII*. For pharmacological testing it was converted to the maleate. Oxidation of *XIII* with excessive hydrogen peroxide in acetic acid at room temperature afforded the sulfoxide *XIV*; it was also converted to the maleate (monohydrate). For preparing the lower homologue *XV*, 2-(phenylthio)benzonitrile (*XVI*) (ref.[21]) was synthesized by reaction of 2--chlorobenzonitrile with thiophenol in refluxing dimethylformamide in the presence of potassium carbonate. Its reaction with hydroxylamine base under various conditions led to mixtures which were separated by chromatography on silica gel. The first to be eluted was the amide *XVII* (ref.[22]) formed by hydrolysis of *XV* and/or *XVI*. The main product, obtained in a moderate yield, was identified as *XV* and converted to the hydrochloride.



XIII, $n = 0$
XIV, $n = 1$



XV, R = —C(=NOH)NH2
XVI, R = CN
XVII, R = $CONH_2$

Compounds *V*–*IX*, *XI*, and *XIII*–*XV* were pharmacologically tested in the form of salts, described in the Experimental; doses were calculated per bases. Acute toxicity in mice, LD_{50} (in mg/kg) on oral adminstration: *VI*, 356; *VII*, 273; *VIII*, 545; *IX*, >1 250; *XIII*, 212; LD_{50} (mg/kg) on i.v. administration: *V*, 25; *XIII*, 100. None of the compounds tested inhibited in concentrations of 100 nmol l^{-1} the binding neither of 4 nmol l^{-1} [^{3}H]imipramine nor of 4 nmol l^{-1} [^{3}H]desipramine to the binding sites in the hypothalamus of the rat brain. Reserpine ptosis in mice was effectively antagonized by *XI* in the oral dose of 30 mg/kg, and by *XIII* in the intraperitoneal dose of 5 mg/kg; following compounds were inactive in doses given (mg/kg orally): *V*, 100; *VII*, 25; *IX*, 25; *XIV*, 100; *XV*, 30. Inhibition of the hypothermic effect of reserpine in mice was found only with *XIII* in intraperitoneal doses of 5–10 mg/kg; compounds *VI*–*IX* were inactive in oral doses of 10 mg/kg. Antagonization of the ulcerogenic effect of reserpine in rats was found only with *VII* in the oral dose of 50 mg/kg. Potentiation of the toxicity of yohimbine inmice: *V*, ED_{50} = 55·3 mg/kg orally (mild effect); *XI* and *XV*, some effect only in sublethal doses of 100 mg/kg orally. Inhibition of the spontaneous locomotor activity of mice in the test of Dews: oral doses of 10 mg/kg of *VI* and *VII* inhibited significantly; the same doses of *VIII*, *IX*, and *XIII* were inactive. In the test of catalepsy in rats,

only *IX* showed some effect: the oral dose of 50 mg/kg elicited catalepsy in 30% animals; *V* and *XIV* in the same doses were inactive. The apomorphine-induced climbing behaviour in mice was not affected by doses of 30 mg/kg orally of *V*, *IX*, *XIV*, and *XV*. Compounds *VI*–*IX* in concentrations of 200 nmol l^{-1} did not affect the binding of 0·5 nmol l^{-1} [^{3}H]spiperone in corpus striatum of the rat brain (no dopaminergic activity). Compound *XIII*, which was subjected to the general pharmacological screening, showed local anaesthetic effect in the concentration of 1% in the test of infiltration anaesthesia in guinea-pigs (procaine-like effect), drops of blood pressure in normotensive rats at 20 mg/kg i.v. or 100 mg/kg orally, antihistamine effect in guinea-pigs at 1 mg/kg s.c. (protected 50% of the animals from the lethal effect of the standard dose of histamine, administered intrajugularly), and antiarrhythmic effect in rats in doses of 10–20 mg/kg i.v. towards aconitine.

In conclusion, only *VII*, *XI*, and *XIII* brought about some antireserpine effects which, however, were not supplemented by activity in the in vitro tests. For this reason, the testing of the whole series was discontinued.

EXPERIMENTAL

The melting points were determined in a Mettler FP-5 melting point recored or in a Kofler block. The samples were dried in vacuo of about 60 Pa over P_2O_5 at room tempeature or at suitably elevated temperature. The UV spectra (in methanol, λ_{max} in nm ($\log \varepsilon$)) were recorded with a Unicam SP 8 000 spectrophotometer, the IR spectra (in Nujol, ν in cm^{-1}) with a Perkin–Elmer 298 spectrophotometer, ^{1}H NMR spectra (in C^2HCl_3 unless stated otherwise, δ, J in Hz) with the Tesla BS 487 C (80 MHz) spectrometer, and the mass spectra with MCH 1 320 and Varian MAT 44S spectrometers (m/z and % given). The homogeneity of the substances and composition of the mixtures were checked by thin-layer chromatography on silica gel (Silufol). The extracts were dried with $MgSO_4$ or K_2CO_3 and evaporated under reduced pressure on a rotating evaporator.

Ethyl (2-(Phenylthio)phenyl)acetimidate (*X*)

A mixture of 45 g (2-(phenylthio)phenyl)acetonitrile[13] and 12 ml ethanol was saturated for 1·5 h with HCl under external cooling (0°C), diluted with 25 ml ether, and allowed to stand overnight at 0°C. The separated hydrochloride of *X* was filtered, washed with 15 ml of a 1 : 3 mixture of ethanol and ether, and dried in vacuo; 37 g (69%), m.p. 110–111°C. For analysis the substance was recrystallized twice from a mixture of ethanol and ether, m.p. 111–112°C, but due to its instability, it was not completely homogeneous. For $C_{16}H_{18}ClNOS$ (307·8) calculated: 62·42% C, 5·89% H, 11·52% Cl, 4·55% N, 10·42% S; found: 61·25% C, 5·92% H, 12·34% Cl, 4·97% N, 10·31% S.

(2-(Phenylthio)phenyl)acetamidine (*V*)

X.HCl (10·0 g) was added under stirring and cooling (0°C) to 50 ml 8% solution of NH_3 in ethanol, the mixture was stirred for 30 min and evaporated under reduced pressure. The residue was treated with 35 ml 10% KOH in ethanol, the mixture was stirred for 30 min, evaporated in vacuo, and the residue was extracted with ether. Processing of the extract gave 7·8 g

(98%) *V*, m.p. 76–77°C (benzene). UV spectrum: 250 (4·04), infl. 275 (3·61). IR spectrum: 688, 745, 750 (5 and 4 adjacent Ar—H); 1 580, 3 040, 3 070 (Ar); 1 602 (C—NH_2); 1 640 (C=N); 3 130, 3 300, 3 440 (NH_2, NH). ^{1}H NMR spectrum: 3·55 s, 2 H ($ArCH_2C$); 5·20 bs, 2 H (NH_2); c. 7·20 m, 10 H (9 ArH and =NH). For $C_{14}H_{14}N_2S$ (242·3) calculated: 69·38% C, 5·82% H, 11·56% N, 13·23% S; found: 68·99% C, 5·85% H, 11·68% N, 13·19% S.

Maleate, m.p. 179–180°C (ethanol). For $C_{18}H_{18}N_2O_4S$ (358·4) calculated: 60·32% C, 5·06% H, 7·82% N, 8·95% S; found: 60·30% C, 5·19% H, 8·04% N, 9·02% S.

Hemimaleate, m.p. 166–168°C (ethanol). For $C_{16}H_{16}N_2O_2S$ (300·3) calculated: 63·99% C, 5·37% H, 9·33% N, 10·70% S; found: 64·09% C, 5·35% H, 9·45% N, 10·72% S.

N,N-Pentamethylene-(2-(phenylthio)phenyl)acetamidine (*VI*)

A mixture of 4·6 g *X*.HCl, 30 ml ethanol, and 1·3 g piperidine was stirred and refluxed for 7 h. Ethanol was evaporated in vacuo, the residue was dissolved in a small amount of ethanol, and the solution was treated with an equal volume of ether; there crystallized 0·20 g piperidine hydrochloride, m.p. 243°C. The mother liquor was diluted with ether which led to crystallization of the hydrochloride of *VI*; 4·28 g (83%), m.p. 131–135°C (ethanol–ether). IR spectrum: 680, 705, 744, 760 (5 and 4 adjacent Ar—H); 1 580, 3 030 (Ar); 1 627, 1 670 (C=NH); 2 730 (NH^+); 3 170, 3 330 (NH). ^{1}H NMR spectrum: 1·60 bm, 6 H (2 H-3, 2 H-4, and 2 H-5 of piperidine); 3·80 bm, 4 H (CH_2NCH_2); 4·30 s, 2 H ($ArCH_2C$); 7·00–7·50 m, 9 H (9 ArH). For $C_{19}H_{23}ClN_2S$ (346·9) calculated: 65·78% C, 6·68% H, 10·22% Cl, 8·08% N, 9·24% S; found: 65·25% C, 6·98% H, 10·18% Cl, 7·53% N, 8·99% S.

N,N-(3-Oxapentane-1,5-diyl)-(2-(phenylthio)phenyl)acetamidine (*VII*)

A mixture of 4·6 g *X*.HCl, 30 ml ethanol, and 1·3 g morpholine was refluxed for 7 h and evaporated in vacuo. The residue was dissolved in 15 ml ethanol and the solution was treated with 100 ml ether; there crystallized 3·55 g (68%) hydrochloride of *VII*, m.p. 195–196°C (ethanol–ether). IR spectrum: 705, 755, 765 (5 and 4 adjacent Ar—H); 1 120 (ROR); 1 615, 1 675 (C=NH); 2 710 (NH^+); 3 170 (NH). ^{1}H NMR spectrum: 3·50 bs, 8 H (2 CH_2N and 2 CH_2O of morpholine); 4·32 s, 2 H ($ArCH_2C$); 7·00–7·50 m, 9 H (9 ArH). For $C_{18}H_{21}ClN_2OS$ (348·9) calculated: 61·96% C, 6·07% H, 10·16% Cl, 8·03% N, 9·19% S; found: 61·79% C, 6·19% H, 10·56% Cl, 8·13% N, 9·23% S.

N,N-(N-Methyl-3-azapentane-1,5-diyl)-(2-(phenylthio)phenyl)acetamidine (*VIII*)

A mixture of 4·6 g *X*.HCl, 30 ml ethanol, and 1·5 g 1-methylpiperazine was refluxed for 7·5 h. The solvent was evaporated in vacuo, the residue was distributed between 20% NaOH and ether, the organic solution was dried, and evaporated. The residue (4·7 g) was dissolved in acetone and the solution was treated with 3·4 g maleic acid. Crystallization of the product from ethanol gave 5·0 g (58%) dimaleate monohydrate, m.p. 173–175°C. Mass spectrum (EI): 325 (M^+, $C_{19}H_{23}N_3S$). IR spectrum: 710, 745 (5 and 4 adjacent Ar—H); 1 675 (C=N); 2 730 (NH^+); 3 020, 3 070 (Ar); 3 420 (NH). For $C_{27}H_{31}N_3O_8S + H_2O$ (575·6) calculated: 56·33% C, 5·78% H, 7·30% N, 5·57% S; found: 56·84% C, 5·78% H, 7·67% N, 5·65% S.

N,N-(N-(2-Hydroxyethyl)-3-azapentane-1,5-diyl)-(2-(phenylthio)phenyl)acetamidine (*IX*)

The preparation was carried out similarly from 5·8 g *X*.HCl and 2·5 g 1-(2-hydroxyethyl)piperazine in 30 ml ethanol. Processing and neutralization with maleic acid gave 6·0 g (53%) dimaleate monohydrate, m.p. 133–135 and 145–148°C (ethanol–acetone). Mass spectrum (EI): 356 (CI),

355 M^+, $C_{20}H_{25}N_3OS$), 225 ($C_{14}H_{11}NS$), 197 ($C_{13}H_9S$), 184 ($C_{12}H_8S$), 178 ($C_{13}H_8N$). For $C_{28}H_{33}N_3O_9S + H_2O$ (605·7) calculated: 55·52% C, 5·83% H, 6·94% N, 5·29% S; found: 55·01% C, 5·88% H, 7·40% N, 5·29% S.

2-(2-(Phenylthio)benzyl)-2-imidazoline (*XI*)

A stirred mixture of 6·0 g (2-(phenylthio)phenyl)acetonitrile[13] and 12·0 g 2-aminoethylammonium toluene-4-sulfonate was heated for 1 h to 200°C. After cooling the melt was diluted with 100 ml water, the mixture was made alkaline with 20% NaOH, and extracted with chloroform. Processing of the extract gave 10·8 g residue which was neutralized with 5·05 g oxalic acid dihydrate in 10 ml acetone. Addition of ether led to precipitation of 2·0 g *XI* oxalate, m.p. 165 to 166°C (ethanol). Mass spectrum: 268 (M^+, $C_{16}H_{16}N_2S$), 197 ($C_{13}H_9S$), 163 ($C_8H_7N_2S$), 159 ($C_{10}H_{11}N_2$). For $C_{18}H_{18}N_2O_4S$ (358·4) calculated: 60·32% C, 5·06% H, 7·82% N, 8·94% S; found: 60·32% C, 5·15% H, 7·93% N, 8·99% S.

The mother liquors after the crystallization of *XI* oxalate were evaporated in vacuo, the residue was decomposed with 20% NaOH, and the bases were extracted with chloroform. Evaporation of the extract gave 5·1 g oily mixture of bases which was chromatographed on 100 g neutral Al_2O_3 (activity II). Elution with benzene afforded further 2·4 g *XI* which was converted to 2·25 g *XI* oxalate (m.p. 165—166°C (ethanol)); the total yield on *XI* oxalate was thus 4·25 g (45%). The elution was continued with chloroform which led to 0·68 g homogeneous N-(2-aminoethyl)-(2-(phenylthio)phenyl)acetamide (*XII*) and afforded 0·69 g hydrogen oxalate, m.p. 172—173°C (ethanol). Mass spectrum: 286 (M^+, $C_{16}H_{18}N_2OS$). IR spectrum: 700, 735, 755 (5 and 4 adjacent Ar—H); 1 520, 1 585, 3 050, 3 065 (Ar); 1 550, 1 660 (RCONHR); 2 495, 2 700 (NH^+); 3 300 (NH, NH_2). For $C_8H_{20}N_2O_5S$ (376·4) calculated: 57·44% C, 5·35% H, 7·44% N, 8·52% S; found: 57·53% C, 5·47% H, 7·53% N, 8·53% S.

(2-(Phenylthio)phenyl)acetamidoxime (*XIII*)

$NH_2OH.HCl$ (9·9 g) was added to a sodium methoxide solution (3·3 g Na in 50 ml methanol), a solution of 27·0 g (2-(phenylthio)phenyl)acetonitrile[13] in 100 ml methanol was added, and the mixture was stirred and refluxed for 5 h. NaCl was filtered off, washed with methanol, and the filtrate was evaporated. The residue (37·4 g) was dissolved in 150 ml chloroform, the solution was washed with water, dried, and evaporated. The residue (28·2 g) crystallized from a mixture of 15 ml benzene and 15 ml hexane giving 13·5 g (44%) *XIII*, m.p. 93—94°C (benzene). IR spectrum: 690, 735, 760 (5 and 4 adjacent Ar—H); 1 470, 1 479, 1 581, 3 070 (Ar); 1 600 (NH_2); 1 666 (C=N); 3 320, 3 445 (NH_2, OH). ^{1}HNMR spectrum ($C^2H_3SOC^2H_3$): 3·00 s, 2 H ($ArCH_2C$); 4·90 bs, 2 H (NH_2); 6·70 m, 9 H (9 ArH); 8·52 s, 1 H (NOH). For $C_{14}H_{14}N_2OS$ (258·3) calculated: 65·09% C, 5·46% H, 10·85% N, 12·41% S; found: 65·37% C, 5·39% H, 10·80% N, 12·70% S.

Maleate, m.p. 140—141°C (ethanol) For $C_{18}H_{18}N_2O_5S$ (374·4) calculated: 57·74% C, 4·85% H, 7·48% N, 8·56% S; found: 57·77% C, 4·84% H, 7·32% N, 8·68% S.

(2-(Phenylthio)phenyl)acetamidoxime S-Oxide (*XIV*)

A solution of 3·9 g *XIII* in 40 ml acetic acid was treated with 1·7 ml 30% H_2O_2. The mixture was allowed to stand for 60 h at room temperature, diluted with 300 ml water, washed with 50 ml benzene, and the aqueous solution was allowed to stand overnight. There crystallized 2·6 g (63%) *XIV*, m.p. 167—168°C (ethanol). Mass spectrum: 274 (M^+, $C_{14}H_{14}N_2O_2S$, 28), 257 ($C_{14}H_{13}N_2OS$, 18), 240 (13), 239 (21), 213 ($C_{13}H_9OS$, 80), 197 ($C_{13}H_9S$, 71), 165 (27),

136 (54), 77 (100). UV spectrum: 234 (4·17), infl. 268 (3·39). IR spectrum: 688, 735, 745, 765 (5 and 4 adjacent Ar—H); 1 015 (S—O); 1 580, 1 590, 3 045 (Ar); 1 620 (NH_2); 1 645 (C=N), 3 200, 3 320, 3 420 (NH_2, OH). ^{1}H NMR spectrum ($C^2H_3SOC^2H_3$): 3·41 d, 1 H and 3·70 d, 1 H (ABq, $ArCH_2C$, J = 13·0); 5·60 bs, 2 H (NH_2); 7·30—7·90 m, 9 H (9 ArH); 9·15 bs, 1 H NOH). For $C_{14}H_{14}N_2O_2S$ (274·3) calculated: 61·29% C, 5·14%H, 10·21% N, 11·69% S; found: 61·34% C, 5·13% H, 9·74% N, 11·81% S.

Maleate monohydrate, m.p. 143—144°C (aqueous ethanol). For $C_{18}H_{18}N_2O_6S + H_2O$ (408·4) calculated: 52·93% C, 4·93% H, 6·86% N, 7·85% S; found: 53·41% C, 4·55% H, 6·68% N, 8·23% S.

2-(Phenylthio)benzonitrile (*XVI*)

A mixture of 13·8 g 2-chlorobenzonitrile, 11·0 g thiophenol, 13·8 g K_2CO_3, and 100 ml dimethylformamide was stirred and refluxed for 15 h in nitrogen atmosphere. The solvent was evaporated in vacuo, the residue was diluted with water, and extracted with benzene. Processing of the extract and distillation of the residue gave 20·7 g (98%) *XVI*, b.p. 215—220°C/70 Pa, m.p. 56·5 to 58°C (cyclohexane–light petroleum). UV spectrum: 253·5 (3·95), infl. 274 (3·63), 315 (3·48). IR spectrum: 690, 750, 770 (5 and 4 adjacent Ar—H); 1 480, 1 588, 3 050 (Ar); 2 225 (Ar—CN). ^{1}H NMR spectrum: 7·00—7·80 m (ArH). For $C_{13}H_9NS$ (211·3) calculated: 73·90% C, 4·29% H, 6·63% N, 15·18% S; found: 74·27% C, 4·49% H, 6·75% N, 15·12% S.

2-(Phenylthio)benzamidoxime (*XV*)

$NH_2OH.HCl$ (4·2 g) and a solution of 12·6 g *XVI* in 60 ml methanol were added to a sodium methoxide solution (1·5 g Na, 30 ml methanol) and the mixture was refluxed for 10 h. NaCl was filtered off and the filtrate was evaporated. The residue was diluted with 250 ml water and extracted with chloroform. Processing of the extract gave 12·2 g inhomogeneous product which was chromatographed on a column of 200 g silica gel. Chloroform eluted first 1·9 g homogeneous 2-(phenylthio)benzamide (*XVII*), m.p. 175—176°C (benzene–ethanol). UV spectrum: 252 (4·02), infl. 274 (3·72). IR spectrum: 690, 750 (5 and 4 adjacent Ar—H); 1 558, 1 580, 3 050 (Ar); 1 618 ($ArCONH_2$); 3 180, 3 270, 3 410 (NH_2). ^{1}H NMR spectrum ($C^2H_3SOC^2H_3$): 6·80—8·00 m; (ArH and $CONH_2$). Ref.[22], m.p. 178°C.

Continued elution with chloroform gave 2·10 g (14%) *XV*, m.p. 132—134°C (benzene). Mass spectrum: 244 (M^+, $C_{13}H_{12}N_2OS$, 23), 227 ($C_{13}H_{11}N_2S$, 100), 210 ($C_{13}H_8NS$, 18), 184, ($C_{12}H_8S$, 20), 109 (60), 93 (54), 77 (46), 51 (50). UV spectrum: 252 (4·10), infl. 275 (3·86).IR spectrum: 690, 736, 754, 765 (5 and 4 adjacent Ar—H); 1 475, 1 572 (Ar); 1 640 (C=N), 3 385, 3 490 (NH_2). ^{1}H NMR spectrum ($C^2H_3SOC^2H_3$): 5·80 bs, 2 H (NH_2); 6·80—7·50 m, 9 H (9 ArH); 9·60 s, 1 H (NOH). For $C_{13}H_{12}N_2OS$ (244·4) calculated: 63·91% C, 4·95% H, 11·47% N, 13·12% S; found: 63·98% C, 4·97% H, 11·70% N, 13·12% S.

Hydrochloride of *XV*, m.p. 162°C (acetone–ether). For $C_{13}H_{13}ClN_2OS$ (280·8) calculated: 55·61% C, 4·66% H, 12·63% Cl, 9·98% N, 11·42% S; found: 55·82% C, 4·60% H, 12·83% Cl, 10·41% N, 11·12% S.

*The authors wish to thank their colleagues at the Research Institute for Pharmacy and Biochemistry for their contributions to the present study: Drs M. Ryska, I. Koruna, J. Schlanger (mass spectra), Dr J. Holubek (*NMR *spectra), Dr E. Svátek, Mrs A. Hrádková, and Mrs Z. Janová (*UV *and* IR *spectra), Mrs J. Komancová, Mrs V. Šmídová, and Mrs J. Kropáčová (elemental analyses), and finally Dr S. Wildt, Dr N. Dlohožková, Mrs S. Schubertová, Miss A. Vykulilová, Mrs M. Jandová, and Mrs A. Kargerová (pharmacological and biochemical screening).*

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Translated by the author (M.P.).