POTENTIAL ANTIDEPRESSANTS: 2-(METHOXY- AND HYDROXY--PHENYLTHIO)BENZYLAMINES AS SELECTIVE INHIBITORS OF 5-HYDROXYTRYPTAMINE RE-UPTAKE IN THE BRAIN

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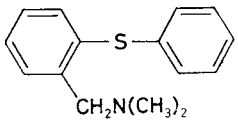
2-, 3- and 4-Methoxythiophenol, and 2,4-, 2,5- and 3,4-dimethoxythiophenol were transformed in two steps to the corresponding 2-(methoxyphenylthio)benzoyl chlorides *XIII* which were reacted with ammonia, methylamine, dimethylamine, diethylamine, dipropylamine, and di(2--propyl)amine to give the amides *XIV*—*XIX*. These were reduced mostly with lithium aluminium hydride to the amines *II*—*VII*. These methoxylated amines were demethylated mostly either by heating with pyridine hydrochloride or by treatment with boron tribromide. Some of the 2--(methoxy- and hydroxy-phenylthio)benzylamines prepared, especially compounds *II*, *III*, *XXI*, and *XXII*, indicated properties of potential antidepressants being highly active and selective inhibitors of 5-hydroxytryptamine re-uptake in the brain structures and having the typical antireserpine activity. The most interesting compound of the series is *XXIb* (hydrogen maleate VÚFB-15 468) which is undergoing preclinical studies. On the basis of its structure, some further compounds (*XXVII*—*XXIX*, *XXXIX*—*XLI*) were prepared by various methods.

In a recent communication[1] we have described the synthesis and some properties of compound *I* which appeared (in the form of maleate) to be a promising potential antidepressant: it is active in two antireserpine tests, potentiates the toxicity of yohimbine, has high affinity to imipramine as well as desipramine binding sites in the rat brain, and inhibits strongly the re-uptake of 5-hydroxytryptamine as well as of noradrenaline in the rat brain structures. We considered worthwile to use the structure *I* as that of a prototype and to start on its basis a broader reseach program in this line with the hope to find within ist structural analogues compounds with even more favourable properties.



I

The first type of analogues selected were derivatives of *I* methoxylated or hydroxylated in the phenylthio residue, i.e. *IIa–IIf* and *XXIa–XXIf* as well as their lower and higher homologues *IIIa–VIIc* and *XXIIa–XXVIc*. Their syntheses started from the coresponding methoxythiophenols which were available by described methods: 2-methoxythiophenol[2], 3-methoxythiophenol[3], 4-methoxythiophenol[4], 2,4--dimethoxythiophenol[5,6], 2,5-dimethoxythiophenol[7], and 3,4-dimethoxythiophenol[8]. These thiophenols were reacted with 2-iodobenzoic acid in a boiling solution of potassium hydroxide in the presence of copper (method *A*) (for the method, cf. ref.[9]). Out of the acids obtained, most are known and three of them were prepared by the same method: *XIa* (refs[10,11]), *XIb* (ref.[12]), *XIc* (ref.[13]), *XIf* (ref.[14]) (different method). The acid *XIb* has now also been obtained by reaction of thiosalicylic acid with 3-bromoanisole in boiling dimethylformamide in the presence of potassium carbonate and copper. The aldehydes *XIIb*, *XIId*, and *XIIe*, also useful as intermediates, were prepared by reactions of 2-chlorobenzaldehyde with the corresponding thiophenols in dimethylformamide in the presence of sodium carbonate or potassium carbonate at 90–120°C. The produts were characterized by spectra and *XIIe* also by the crystalline semicarbazone. Compounds described in this paper, which were obtained by general methods, are assembled in Table I with the usual experimental data. Their spectral data are assembled in Table II. The Experimental describes only examples of the individual general methods and experiments in which the general methods were not used.

The acids *XIa–XIf* were transformed to the acid chlorides *XIIIa–XIIIf* by treatment with thionyl chloride in boiling benzene in the presence of a small quantity of dimethylformamide (method *B*). All of them are relatively stable crystalline substances which could be characterized by spectra. Only *XIIIc* was described as a characterized compound[15]; the preparation of *XIIIa* was described[10,11] but the product was mentioned only as an oil. Treatment of the benzene solutions of *XIIIa* to *XIIIf* with 20–25% aqueous solutions of ammonia, methylamine or dimethylamine under vigorous stirring (method *C-1*) resulted in the amides *XIVa–XIVf*, *XVa–XVf*, and *XVIa–XVIf*. Only the amides *XIVa* and *XVIa* were prepared formerly[10] by a similar method. The dimethylamide *XVIb* was also prepared by further modified procedures: (i) by saturation of a benzene solution of *XIIIb* with gaseous dimethylamine and (ii) by treatment of an aqueous solution of dimethylamine hydrochloride with aqueous sodium hydroxide and by stirring the mixture with a toluene solution of *XIIIb*. All the amides, methylamides, and dimethylamides were crystalline and were characterized by spectra. Reactions of *XIIIa–XIIIc* with diethylamine, dipropylamine, and di(2-propyl)amine in benzene solutions (method *C-2*) gave the amides *XVIIa–XIXc*. Only *XVIIa*, *XIXa*, and *XIXb* were crystalline and could be fully characterized. The other (*XVIIb*, *XVIIc*, *XVIIIa–XVIIIc*, and *XIXc*) were oily and were further processed without characterization. In one case (attempt to prepare *XVIIb* by method *C-2*), when the used *XIIIb* was allowed to stand at

TABLE I

2-(Methoxy- and hydroxy-phenylthio)benzylamines and intermediates

Compound[a]	Method (yield, %)	M.p., °C (solvent)	Formula (M.w.)	Calculated/Found				
				% C	% H	% Hal	% N	% S
XIa	*A* (93)	198–200[b] (aqueous ethanol)						
XIb	*A* (90)	171–171·5[c] (aqueous ethanol)						
XIc	*A* (88)	238–240[d] (ethanol)						
XId	*A*[e] (84)	215–217 (ethanol)	$C_{15}H_{14}O_4S$ (290·3)	62·05 62·17	4·86 4·95	— —	— —	11·04 11·00
XIe	*A* (94)	204–205 (ethanol)	$C_{15}H_{14}O_4S$ (290·3)	62·05 62·27	4·86 5·03	— —	— —	11·04 10·86
XIf	*A* (89)	215–217[f] (ethanol)	$C_{15}H_{14}O_4S$ (290·3)	62·05 61·95	4·86 4·90	— —	— —	11·04 11·28
XIIIa	*B* (96)	96·5[g] (cyclohexane)	$C_{14}H_{11}ClO_2S$ (278·7)	60·32 60·02	3·98 4·01	12·72 12·79	— —	11·50 11·25
XIIIb	*B*[e] (96)	101–101·5 (cyclohexane)	$C_{14}H_{11}ClO_2S$ (278·7)	60·32 60·38	3·98 3·94	12·72 13·06	— —	11·50 11·38
XIIIc	*B* (95)	94–95[h] (cyclohexane)						
XIIId	*B* (95)	119–121 (cyclohexane)	$C_{15}H_{13}ClO_3S$ (308·8)	58·34 58·64	4·24 4·39	11·48 11·30	— —	10·39 10·20

XIIIe	*B*	101—102	$C_{15}H_{13}ClO_3S$	58·34	4·24	11·48	—	10·39
	(91)	(cyclohexane)	(308·8)	58·34	4·29	11·18	—	10·33
XIIIf	*B*	133—134	$C_{15}H_{13}ClO_3S$	58·34	4·24	11·48	—	10·39
	(82)	(benzene–cyclohexane)	(308·8)	58·70	4·33	11·55	—	10·36
XIVa	*C-1*	131[i]						
	(95)	(ethanol)						
XXIVb	*C-1*	120·5	$C_{14}H_{13}NO_2S$	64·85	5·05	—	5·40	12·36
	(94)	(ethanol)	(259·3)	65·05	5·09	—	5·42	12·24
XIVc	*C-1*	178	$C_{14}H_{13}NO_2S$	64·85	5·05	—	5·40	12·36
	(98)	(ethanol)	(259·3)	65·11	5·07	—	5·32	12·60
XIVd	*C-1*	164·5—165·5	$C_{15}H_{15}NO_3S$	62·26	5·23	—	4·84	11·08
	(89)	(ethanol)	(289·3)	62·06	5·29	—	4·92	11·34
XIVe	*C-1*	151—152	$C_{15}H_{15}NO_3S$	62·26	5·23	—	4·84	11·08
	(94)	(ethanol)	(289·3)	62·18	5·21	—	4·76	11·19
XVIf	*C-1*	179	$C_{15}H_{15}NO_3S$	62·26	5·23	—	4·84	11·08
	(98)	(ethanol)	(289·3)	62·52	5·33	—	4·77	11·39
XVa	*C-1*	109—110	$C_{15}H_{15}NO_2S$	65·91	5·53	—	5·12	11·73
	(90)	(ethanol)	(273·3)	65·74	5·68	—	4·98	11·91
XVb	*C-1*	92	$C_{15}H_{15}NO_2S$	65·91	5·53	—	5·12	11·73
	(87)	(aqueous ethanol)	(273·3)	65·99	5·41	—	5·12	11·90
XVc	*C-1*	140·5—141	$C_{15}H_{15}NO_2S$	65·91	5·53	—	5·12	11·73
	(93)	(ethanol)	(273·3)	65·98	5·66	—	5·14	11·83
XVd	*C-1*	151—152	$C_{16}H_{17}NO_3S$	63·34	5·65	—	4·62	10·57
	(93)	(benzene–light petroleum)	(303·4)	63·33	5·72	—	4·58	10·26
XVe	*C-1*	82—83	$C_{16}H_{17}NO_3S$	63·34	5·65	—	4·62	10·57
	(99)	(benzene–light petroleum)	(303·4)	63·41	5·70	—	4·38	10·53

TABLE I
(*Continued*)

Compound[a]	Method (yield, %)	M.p., °C (solvent)	Formula (M.w.)	Calculated/Found				
				% C	% H	% Hal	% N	% S
XVf	*C-1* (89)	146 (ethanol)	$C_{16}H_{17}NO_3S$ (303·4)	63·34 63·58	5·65 5·76	— —	4·62 4·72	10·57 10·71
XVIa	*C-1* (96)	95[j] (ethanol–light petroleum)						
XVIb	*C-1*[e] (93)	42—43 (light petroleum)	$C_{16}H_{17}NO_2S$ (287·4)	66·87 67·17	5·96 6·11	— —	4·87 5·02	11·16 10·93
XVIc	*C-1* (80)	81·5 (cyclohexane)	$C_{16}H_{17}NO_2S$ (287·4)	66·87 66·88	5·96 6·03	— —	4·87 4·93	11·16 11·06
XVId	*C-1* (98)	126—127 (benzene)	$C_{17}H_{19}NO_3S$ (317·4)	64·33 64·15	6·03 6·10	— —	4·41 4·49	10·10 10·25
XVIe	*C-1* (98)	72—73 (benzene–light petroleum)	$C_{17}H_{19}NO_3S$ (317·4)	64·33 64·18	6·03 6·06	— —	4·41 4·32	10·10 10·30
XVIf	*C-1* (95)	119—120 (ethanol)	$C_{17}H_{19}NO_3S$ (317·4)	64·33 64·44	6·03 5·88	— —	4·41 4·48	10·10 9·99
XVIIa	*C-2* (91)	87—89 (aqueous ethanol)	$C_{18}H_{21}NO_2S$ (315·4)	68·54 68·09	6·71 6·58	— —	4·44 4·37	10·17 10·34
XVIIb	*C-2* (95)	oil						
XVIIc	*C-2* (95)	oil						

XVIIIa	*C-2* (94)	oil						
XVIIIb	*C-2* (88)	oil						
XVIIIc	*C-2* (97)	oil						
XIXa	*C-2* (83)	121—123 (cyclohexane)	$C_{20}H_{25}NO_2S$ (343·5)	69·93 70·04	7·34 7·20	— —	4·08 3·77	9·33 9·62
XIXb	*C-2*[e] (76)	98—100 (benzene–hexane)	$C_{20}H_{25}NO_2S$ (343·5)	69·93 70·05	7·34 7·68	— —	4·08 3·88	9·33 9·65
XIXc	*C-2* (95)	oil						
IIa-HCl	*D-1* (83)	174—175 (ethanol–ether)	$C_{16}H_{20}ClNOS$ (309·8)	62·02 62·03	6·51 6·51	11·44 11·59	4·52 4·52	10·35 10·53
IIb-HCl	*D-1*[e] (93)	149—150 (ethanol–ether)	$C_{16}H_{20}ClNOS$ (309·8)	62·02 62·08	6·51 6·49	11·44 11·58	4·52 4·60	10·35 10·56
IIc	*D-1* (94)	60 (light petroleum)	$C_{16}H_{19}NOS$ (273·4)	70·29 70·47	7·01 7·04	— —	5·12 5·10	11·73 11·49
IIc-HCl		158—159 (ethanol–ether)	$C_{16}H_{20}ClNOS$ (309·8)	62·02 61·89	6·51 6·51	11·44 11·51	4·52 4·46	10·35 10·53
IId-HM	*D-1* (82)	117—118 (ethanol–ether)	$C_{21}H_{25}NO_6S$ (419·5)	60·12 60·52	6·01 6·05	— —	3·34 3·54	7·64 7·58
IId-HBr		208—209 (ethanol)	$C_{17}H_{22}BrNO_2S$ (384·3)	53·12 53·06	5·77 6·05	20·30 20·30	3·64 4·16	8·34 8·31
IIe-HM	*D-1* (91)	101—103 (ethanol)	$C_{21}H_{25}NO_6S$ (419·5)	60·12 60·10	6·01 6·10	— —	3·34 3·26	7·64 7·93
IIf-HCl	*D-2*[e] (86)	175—176 (ethanol–ether)	$C_{17}H_{22}ClNO_2S$ (339·9)	60·07 60·48	6·53 6·67	10·43 10·63	4·12 3·87	9·43 9·69

TABLE I
(*Continued*)

Compound[a]	Method (yield, %)	M.p., °C (solvent)	Formula (M.w.)	Calculated/Found				
				% C	% H	% Hal	% N	% S
IIIa-HCl	*D-1* (81)	181—182 (ethanol)	$C_{15}H_{18}ClNOS$ (295·8)	60·90 61·02	6·12 6·24	11·99 11·98	4·73 4·71	10·84 10·62
IIIb-HCl	*D-1* (88)	130 (ethanol–ether)	$C_{15}H_{18}ClNOS$ (295·8)	60·90 61·07	6·12 6·11	11·99 12·16	4·73 4·91	10·84 10·84
IIIc-HCl	*D-1* (92)	133—134 (ethanol–ether)	$C_{15}H_{18}ClNOS$ (295·8)	60·90 60·72	6·12 6·16	11·99 12·09	4·73 4·75	10·84 11·00
IIId	*D-1* (88)	46—47 (benzene–hexane)	$C_{16}H_{19}NO_2S$ (289·4)	66·40 66·69	6·62 6·53	— —	4·84 4·76	11·08 10·87
IIId-HM		137—138 (ethanol)	$C_{20}H_{23}NO_6S$ (405·5)	59·24 58·80	5·72 5·83	— —	3·45 3·54	7·91 8·18
IIIe-HM	*D-1* (95)	119—121 (ethanol)	$C_{20}H_{23}NO_6S$ (405·5)	59·24 59·17	5·72 5·87	— —	3·45 3·42	7·91 7·73
IIIf-HM	*D-2* (82)	151—152 (ethanol)	$C_{20}H_{23}NO_6S$ (405·4)	59·24 59·44	5·72 5·88	— —	3·45 3·51	7·91 8·06
IVa	*D-1* (77)	50—51 (cyclohexane)	$C_{14}H_{15}NOS$ (245·3)	68·54 68·41	6·16 6·22	— —	5·71 5·74	13·07 13·18
IVa-HCl		213—214 (ethanol)	$C_{14}H_{16}ClNOS$ (281·8)	59·67 60·07	5·72 5·79	12·58 12·82	4·97 4·99	11·38 11·46
IVb-HCl	*D-1* (70)	161—162 (ethyl acetate)	$C_{14}H_{16}ClNOS$ (281·8)	59·67 59·47	5·72 5·79	12·58 12·48	4·97 4·99	11·38 11·32
IVc-HCl	*D-1* (73)	182—182·5 (ethanol)	$C_{14}H_{16}ClNOS$ (281·8)	59·67 59·76	5·72 5·72	12·58 12·74	4·97 4·87	11·38 11·30

IVd	*D-1* (78)	71—72 (benzene–light petroleum)	$C_{15}H_{17}NO_2S$ (275·4)	65·42 65·53	6·22 6·30	— —	5·09 5·16	11·65 11·61
IVd-HM		112—113 (ethanol)	$C_{19}H_{21}NO_6S$ (391·4)	58·30 58·42	5·41 5·56	— —	3·58 3·42	8·19 8·20
IVe	*D-1* (88)	76—77 (benzene–light petroleum)	$C_{15}H_{17}NO_2S$ (275·4)	65·42 65·73	6·22 6·36	— —	5·09 5·03	11·65 11·78
IVe-HM		149—151 (ethanol)	$C_{19}H_{21}NO_6S$ (391·4)	58·30 58·60	5·41 5·56	— —	3·58 3·40	8·19 8·04
IVf	*D-1* (52)	68—68·5 (cyclohexane)	$C_{15}H_{17}NO_2S$ (275·4)	65·42 65·71	6·22 6·35	— —	5·09 5·02	11·65 11·87
IVf-HCl		212—213 (ethanol)	$C_{15}H_{18}ClNO_2S$ (311·8)	57·78 57·99	5·82 5·85	11·37 11·55	4·49 4·40	10·28 10·30
Va-HCl	*D-3*[e] (74)	182—184 (ethanol–ether)	$C_{18}H_{24}ClNOS$ (337·9)	63·98 63·96	7·16 6·99	10·49 10·57	4·14 3·96	9·49 9·55
Vb	*D-3* (71)	b.p. 160—162°C/ /0·13 kPa	$C_{18}H_{23}NOS$ (301·4)	71·71 71·81	7·69 7·95	— —	4·65 4·76	10·64 10·47
Vc-HCl	*D-3* (62)	151—153 (ethanol–ether)	$C_{18}H_{24}ClNOS$ (337·9)	63·98 63·81	7·16 7·40	10·49 10·79	4·14 4·42	9·49 9·74
VIa-HCl	*D-3* (80)	173—175 (ethanol–ether)	$C_{20}H_{28}ClNOS$ (366·0)	65·64 65·51	7·71 7·75	9·69 9·65	3·83 3·94	8·76 9·01
VIb	*D-3* (62)	b.p. 165—168°C/ /0·13 kPa	$C_{20}H_{27}NOS$ (329·5)	72·90 72·64	8·26 8·40	— —	4·25 4·24	9·73 9·72
VIc-HCl	*D-3* (69)	152—154 (ethanol–ether)	$C_{20}H_{28}ClNOS$ (366·0)	65·64 65·93	7·71 7·95	9·69 9·83	3·83 3·64	8·76 8·77
VIIa-HCl	*D-3* (86)	182—184 (ethanol–ether)	$C_{20}H_{28}ClNOS$ (366·0)	65·64 65·61	7·71 7·56	9·69 9·61	3·83 3·77	8·76 8·83

TABLE I
(*Continued*)

Compound	Method (yield, %)	M.p., °C (solvent)	Formula (M.w.)	Calculated/Found				
				% C	% H	% Hal	% N	% S
VIIb	*D-3* (70)	b.p. 172–175°C/ /0·13 kPa	$C_{20}H_{27}NOS$ (329·5)	72·90 72·79	8·26 8·29	— —	4·25 4·19	9·73 9·70
VIIc-HCl	*D-3* (81)	148–150 (acetone–ether)	$C_{20}H_{28}ClNOS$ (366·0)	65·64 65·42	7·71 7·71	9·69 9·97	3·83 3·63	8·76 8·76
XXIa	*E* (78)	83·5 (ethanol)	$C_{15}H_{17}NOS$ (259·4)	69·46 69·16	6·61 6·76	— —	5·40 5·28	12·36 12·47
XXIa-HM		107–108 (ethanol–ether)	$C_{19}H_{21}NO_5S$ (375·4)	60·78 60·61	5·64 5·63	— —	3·73 3·51	8·54 8·80
XXIb	*E*[e] (84)	106–107 (cyclohexane)	$C_{15}H_{17}NOS$ (259·4)	69·46 69·19	6·61 6·76	— —	5·40 5·28	12·36 12·11
XXIb-HM		123–124 (ethanol–ether)	$C_{19}H_{21}NO_5S$ (375·4)	60·78 61·12	5·64 5·82	— —	3·73 3·79	8·54 8·46
XXIb-HBr	*F*[e] (75)	150–151 (ethanol–ether)	$C_{15}H_{18}BrNOS$ (340·3)	52·94 52·96	5·33 5·29	23·49 23·38	4·12 4·14	9·42 9·47
XXIb-HCl		165–166 (ethanol)	$C_{15}H_{18}ClNOS$ (295·8)	60·90 60·97	6·13 6·07	11·99 12·16	4·73 4·80	10·84 10·97
XXIc	*E* (83)	119–121 (cyclohexane)	$C_{15}H_{17}NOS$ (259·4)	69·46 69·21	6·61 6·78	— —	5·40 5·15	12·36 12·45
XXIc-HM		153–154 (ethanol)	$C_{19}H_{21}NO_5S$ (375·4)	60·78 60·72	5·64 5·71	— —	3·73 3·79	8·54 8·68

XXId	*F* (64)	166—170 (benzene)	$C_{15}H_{17}NO_2S$ (275·4)	65·43 65·16	6·23 6·11	—	5·08 5·31	11·64 11·66
XXId-HM[k]		141 (ethanol)	$C_{19}H_{21}NO_6S$. 2 H_2O (427·4)	53·39 53·18	5·90 5·43	—	3·28 3·09	7·49 7·41
XXIe	*F* (74)	126—127 (ethanol)	$C_{15}H_{17}NO_2S$ (275·4)	65·43 64·80	6·23 6·02	—	5·08 5·16	11·64 11·90
XXIe-HM		159 (ethanol)	$C_{19}H_{21}NO_6S$ (391·4)	58·30 58·36	5·41 5·36	—	3·57 3·59	8·19 8·43
XXIf	*F* (80)	149—152 (ethanol)	$C_{15}H_{17}NO_2S$ (275·4)	65·43 65·13	6·23 6·21	—	5·08 5·36	11·64 11·38
XXIf-HM		152—153 (ethanol–ether)	$C_{19}H_{21}NO_6S$ (391·4)	58·30 58·32	5·41 5·68	—	3·57 3·42	8·19 8·03
XXIIa	*E* (61)	117—118 (ethanol)	$C_{14}H_{15}NOS$ (245·3)	68·54 68·77	6·16 6·29	—	5·71 5·81	13·07 12·89
XXIIa-HM		169 (ethanol)	$C_{18}H_{19}NO_5S$ (361·4)	59·82 59·94	5·30 5·44	—	3·87 3·93	8·87 8·99
XXIII	*E* (81)	142—143 (ethanol–cyclohexane)	$C_{14}H_{15}NOS$ (245·3)	68·54 68·34	6·16 6·28	—	5·71 5·66	13·07 13·07
XXIIb-HM		138—139 (ethanol–ether)	$C_{18}H_{19}NO_5S$ (361·4)	59·82 60·00	5·30 5·42	—	3·87 3·95	8·87 9·06
XXIIc	*E* (86)	129—131 (ethanol–light petroleum)	$C_{14}H_{15}NOS$ (245·3)	68·54 68·24	6·16 6·20	—	5·71 5·71	13·07 12·83
XXIIc-HM		143—143·5 (ethanol)	$C_{18}H_{19}NO_5S$ (361·4)	59·82 59·92	5·30 5·35	—	3·87 4·02	8·87 9·24

TABLE I
(*Continued*)

Compound[a]	Method (yield, %)	M.p., °C (solvent)	Formula (M.w.)	Calculated/Found				
				% C	% H	% Hal	% N	% S
XXIId	*F* (50)	195 (ethanol–light petroleum)	$C_{14}H_{15}NO_2S$ (261·3)	64·34 64·23	5·79 5·88	— —	5·36 5·60	12·26 12·39
XXIId-HBr		225—226 (ethanol)	$C_{14}H_{16}BrNO_2S$ (342·3)	49·13 49·41	4·71 4·72	23·35 23·43	4·09 4·27	9·37 9·45
XXIIe	*F* (75)	168—172 (ethanol)	$C_{14}H_{15}NO_2S$ (261·3)	64·34 64·05	5·79 5·67	— —	5·36 5·50	12·26 12·16
XXIIe-HM		163—164 (ethanol)	$C_{18}H_{19}NO_6S$ (377·4)	57·28 57·16	5·07 5·21	— —	3·71 4·01	8·49 8·66
XXIIf	*F* (73)	85—86 (ethanol)	$C_{14}H_{15}NO_2S$ (261·3)	64·34 64·31	5·79 5·81	— —	5·36 5·56	12·26 12·35
XXIIf-HM		160 (ethanol-ether)	$C_{18}H_{19}NO_6S$ (377·4)	57·28 57·22	5·07 5·27	— —	3·71 3·72	8·49 8·58
XXIIIa	*E* (69)	150—151·5 (ethanol)	$C_{13}H_{13}NOS$ (231·3)	67·51 67·26	5·66 5·71	— —	6·05 5·84	13·86 13·76
XXIIIa-HCl		256—258 (ethanol–light petroleum)	$C_{13}H_{14}ClNOS$ (267·8)	58·31 58·43	5·27 5·23	13·24 13·13	5·23 5·28	11·97 12·17
XXIIIa-HM		187—187·5 (ethanol)	$C_{17}H_{17}NO_5S$ (347·4)	58·78 58·72	4·93 4·83	— —	4·03 4·11	9·23 9·38
XXIIIb	*E* (31)	127—128 (ethanol–light petroleum)	$C_{13}H_{13}NOS$ (231·3)	67·51 67·82	5·66 5·81	— —	6·05 5·88	13·86 13·83

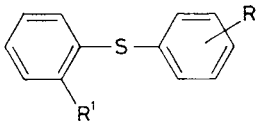
XXIIIb-HM		144·5 (ethanol–ether)	$C_{17}H_{17}O_5S$ (347·4)	58·78 58·99	4·93 5·16	— —	4·03 4·32	9·23 9·56
XXIIIc	*E* (80)	162—163 (ethanol)	$C_{13}H_{13}NOS$ (231·3)	67·51 67·56	5·66 5·62	— —	6·05 6·12	13·86 13·64
XXIIIc[1]		154 (aqueous ethanol)	$C_{17}H_{17}NO_5S + 0{\cdot}5\,H_2O$ (356·4)	57·30 57·60	5·09 5·08	— —	3·92 3·99	9·00 9·30
XXIIIe	*F* (67)	148—150 (ethanol)	$C_{13}H_{13}NO_2S$ (247·3)	63·14 62·84	5·30 5·11	— —	5·66 5·85	12·96 12·73
XXIIIe-HM		150—151 (ethanol)	$C_{17}H_{17}NO_6S$ (363·4)	56·19 55·89	4·72 4·76	— —	3·85 4·07	8·82 8·94
XXIIIf	*F* (73)	139—141 (ethanol)	$C_{13}H_{13}NO_2S$ (247·3)	63·14 62·92	5·30 5·37	— —	5·66 5·73	12·96 12·80
XXIIIf-HBr		191—192 (ethanol–ether)	$C_{13}H_{14}BrNO_2S$ (328·2)	47·57 47·34	4·30 4·44	24·35 24·08	4·26 4·33	9·77 9·78
XXIVa-HCl	*E* (31)	166—168 (ethanol)	$C_{17}H_{22}ClNOS$ (323·9)	63·04 62·97	6·85 6·93	10·95 10·98	4·32 4·32	9·90 9·84
XXIVb-HCl	*E* (56)	155—157 (ethanol–ether)	$C_{17}H_{22}ClNOS$ (323·9)	63·04 62·76	6·85 6·91	10·95 10·93	4·32 4·27	9·90 10·22
XXIVc-HCl	*E* (35)	190—192 (ethanol)	$C_{17}H_{22}ClNOS$ (323·9)	63·04 63·00	6·85 6·88	10·95 10·95	4·32 4·17	9·90 9·81
XXVa-HCl	*E* (50)	225—227 (ethanol–ether)	$C_{19}H_{26}ClNOS$ (351·9)	64·85 64·49	7·44 7·61	10·07 10·15	3·98 3·93	9·12 9·11
XXVb-HCl	*E* (72)	204—206 (ethanol–ether)	$C_{19}H_{26}ClNOS$ (351·9)	64·84 64·46	7·44 7·49	10·07 10·17	3·98 3·80	9·12 9·20
XXVc-HCl	*F* (64)	226—228 (aqueous ethanol)	$C_{19}H_{26}ClNOS$ (351·9)	64·84 64·70	7·44 7·39	10·07 10·52	3·98 4·10	9·12 9·11

TABLE I
(*Continued*)

Compound[a]	Method (yield, %)	M.p., °C (solvent)	Formula (M.w.)	Calculated/Found				
				% C	% H	% Hal	% N	% S
XXVIa	*F*	83–85	$C_{19}H_{25}NOS$	72·33	8·00	—	4·44	10·16
	(55)	(aqueous methanol)	(315·5)	72·41	7·87	—	4·47	9·97
XXVIa-HCl		198–200	$C_{19}H_{26}ClNOS$	64·84	7·44	10·07	3·98	9·12
		(ethanol–ether)	(351·9)	64·90	7·52	10·01	3·72	9·23
XXVIb-HBr	*F*	181–183	$C_{19}H_{26}BrNOS$	57·57	6·61	20·16	3·53	8·09
	(77)	(ethanol–ether)	(396·4)	57·33	6·68	20·20	3·47	8·00
XXVIb-HCl		191–193	$C_{19}H_{26}ClNOS$	64·84	7·44	10·07	3·97	9·12
		(ethanol)	(351·9)	64·92	7·51	9·78	3·93	9·13
XXVIc-HCl	*F*	200–202	$C_{19}H_{26}ClNOS$	64·84	7·44	10·07	3·98	9·12
	(73)	(ethanol–ether)	(351·9)	65·04	7·57	10·10	3·77	8·98

[a] HM hydrogen maleate; [b] ref.[10], m.p. 200–201°C; [c] ref.[12], m.p. 173–174°C; [d] ref.[13], m.p. 240·5–243°C; [e] see Experimental; [f] ref.[14], m.p. 212–213°C (different method); [g] refs[10,11], noncharacterized oil; [h] ref.[15], m.p. 96–97°C; [i] ref.[10], m.p. 132·5–133·5°C; [j] ref.[10], m.p. 94 to 96°C; [k] dihydrate; [l] hemihydrate.

room temperature for a longer time (several weeks), a nitrogen-free product was obtained which was identified as *XXXII*. The chloride *XIIIb* evidently underwent during storing the spontaneous cyclization. Compound *XXXII* was mentioned only in one patent[16].

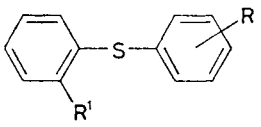


II, $R^1 = CH_2N(CH_3)_2$
III, $R^1 = CH_2NHCH_3$
IV, $R^1 = CH_2NH_2$
V, $R^1 = CH_2N(C_2H_5)_2$
VI, $R^1 = CH_2N(CH_2CH_2CH_3)_2$
VII, $R^1 = CH_2N(CH(CH_3)_2)_2$
VIII, $R^1 = CHN(CH_3)_2$ (CH_3)
IX, $R^1 = CH_2NH(CH_2)_2N(CH_3)_2$
X, $R^1 = CH_2N(CH_2)_2N(CH_3)_2$ (CH_3)

XI, $R^1 = COOH$
XII, $R^1 = CHO$
XIII, $R^1 = COCl$
XIV, $R^1 = CONH_2$
XV, $R^1 = CONHCH_3$
XVI, $R^1 = CON(CH_3)_2$
XVII, $R^1 = CON(C_2H_5)_2$
XVIII, $R^1 = CON(CH_2CH_2CH_3)_2$
XIX, $R^1 = CON(CH(CH_3)_2)_2$
XX, $R^1 = CONH(CH_2)_2N(CH_3)_2$

In formulae *II*–*XX*: *a*, R = 2-OCH_3 *b*, R = 3-OCH_3 *c*, R = 4-OCH_3
d, R = 2,4-$(OCH_3)_2$ *e*, R = 2,5-$(OCH_3)_2$ *f*, R = 3,4-$(OCH_3)_2$

The amides just mentioned were reduced with lithium aluminium hydride either in ether (method *D-1*), or – due to poor solubility – in tetrahydrofuran (method *D-2*) or in a mixture of ether and benzene (method *D-3*). Only a part of the amines *II*–*VII* obtained is crystalline; most of them are oily. All bases were transformed



XXI, $R^1 = CH_2N(CH_3)_2$
XXII, $R^1 = CH_2NHCH_3$
XXIII, $R^1 = CH_2NH_2$
XXIV, $R^1 = CH_2N(C_2H_5)_2$
XXV, $R^1 = CH_2N(CH_2CH_2CH_3)_2$
XXVI, $R^1 = CH_2N(CH(CH_3)_2)_2$

XXVII, $R^1 = CHN(CH_3)_2$ (CH_3)
XXVIII, $R^1 = CH_2NH(CH_2)_2N(CH_3)_2$
XXIX, $R^1 = CH_2N(CH_2)_2N(CH_3)_2$ (CH_3)
XXX, $R^1 = COOH$
XXXI, $R^1 = CON(CH_3)_2$

In formulae *XXI*–*XXXI* *a*, R = 2-OH *b*, R = 3-OH *c*, R = 4-OH
d, R = 2,4-$(OH)_2$ *e*, R = 2,5-$(OH)_2$ *f*, R = 3,4-$(OH)_2$

TABLE II

Spectra of 2-(methoxy- and hydroxy-phenylthio)benzylamines and intermediates

Compound	Spectrum	Data
XId	UV	223 (4·43), infl. 237 (4·22), 255·5 (4·05), 281 (3·83), infl. 289 (3·81), 320 (3·69)
	IR	745, 800, 830, 869 (4 and 2 adjacent and solitary Ar–H); 935, 1 210, 1 250, 1 660, 2 560, 2 645, infl. 3 100 (ArCOOH); 1 030, 1 210, 1 250 ($ArOCH_3$); 1 483, 1 555, 1 571, 1 600 (Ar)
	^{1}H NMR[a]	3·71 s and 3·81 s, 3 + 3 H (2 OCH_3); 6·50–6·80 m, 3 H (H-3′, H-5′, H-6′); 7·00–7·50 m, 3 H (H-3, H-4, H-5); 7·90 dd, 1 H (H-6, J = 8·5; 2·0)
XIe	UV	255 (3·88), 315 (3·93)
	IR	748, 793, 885 (4 and 2 adjacent and solitary Ar–H); 906, 1 259, 1 270, 1 300, 1 674, 2 515, 2 570, 2 650, infl. 3 100 (ArCOOH); 1 040 ($ArOCH_3$); 1 476, 1 487, 1 558, 1 587, 1 600, 3 000, 3 060 (Ar)
	^{1}H NMR[a]	3·63 s and 3·68 s, 3 + 3 H (2 OCH_3); 6·60–7·50 m, 6 H (H-3, H-4, H-5, H-3′, H-4′, H-6′); 7·90 m, 1 H (H-6)
XIf	UV	247 (4·43), infl. 252 (4·02), infl. 285 (3·84), 320 (3·70)
	IR	750, 800, 880 (4 and 2 adjacent and solitary Ar–H); 934, 1 232, 1 269, 1 670, 2 555, 2 640, 3 120 (ArCOOH); 1 030, 1 251 ($ArOCH_3$); 1 504, 1 556, 1 585 (Ar)
	^{1}H NMR[a]	3·73 s and 3·81 s, 3 + 3 H (2 OCH_3); 6·70 dd, 1 H (H-3, J = 9·0; 2·0); 7·00–7·50 m, 5 H (H-4, H-5, H-2′, H-5′, H-6′); 7·90 dd, 1 H (H-6, J = 9·0; 2·0)
XIIIa	UV	255 (3·90), 281 (3·73), 288 (3·72), 321 (3·71)
	IR	696, 866 (C–Cl); 753, 770 (4 adjacent Ar–H); 1 250, 1 275 ($ArOCH_3$); 1 475, 1 554, 1 580, 1 589, 3 046, 3 065, 3 093 (Ar); 1 723, 1 756 (ArCOCl)
XIIIb	UV	224 (4·41), 253 (3·99), 280 (3·79), 320 (3·74)
	IR	692, 725, 780, 790, 850, 860, 879 (4 and 3 adjacent and solitary Ar–H); 1 031, 1 130, 1 187, 1 250 ($ArOCH_3$); 1 480, 1 550, 1 588, 3 000, 3 060, 3 080 (Ar); infl. 1 725, 1 757 (ArCOCl)
	^{1}H NMR	3·79 s, 3 H (OCH_3); 6·70–7·50 m, 7 H (H-3, H-4, H-5, H-2′, H-4′, H-5′, H-6′); 8·21 m, 1 H (H-6)
XIIId	UV	infl. 255 (4·04), 281 (3·77), infl. 288 (3·74), 3·24 (3·72)
	IR	745, 830, 865 (4 and 2 adjacent and solitary Ar–H); 1 030, 1 080, (1 165, 1 215 ($ArOCH_3$); 1 488, 1 555, 1 575, 1 598, 3 010, 3 060 (Ar); 1 720, 1 760 (ArCOCl)

XIIIf	UV	224 (4·42), infl. 257 (4·03), infl. 280 (3·82), 322 (3·73)
	IR	694, 855 (C–Cl); 765, 775, 800, 873 (4 and 2 adjacent and solitary Ar–H); 1 231, 1 256 ($ArOCH_3$); 1 500, 1 550, 1 583, 3 000, 3 072 (Ar), 1 759 (ArCOCl)
XIVa	^{1}H NMR	3·70 s, 3 H (OCH_3); 6·60 bs, 2 H (NH_2); 6·70—7·40 m, 7 H (ArH with the exception of H-6); 7·65 m, 1 H (H-6)
XIVb	UV	252 (3·99), 283 (3·83)
	IR	739, 750, 779, 891 (4 and 3 adjacent and solitary Ar–H); 1 043, 1 232, 1 286 ($ArOCH_3$); 1 560, 1 578, 1 590, 3 055 (Ar), 1 625 ($ArCONH_2$); 3 180, 3 408, 3 420 (NH_2)
	^{1}H NMR[a]	3·70 s, 3 H (OCH_3); 6·80—7·60 m, 8 H (ArH); 7·50 bs and 7·90 bs 1 + 1 H ($CONH_2$)
XIVc	UV	226 (4·31), 252·5 (4·10), infl. 302 (3·55)
	IR	744, 829 (4 and 2 adjacent Ar–H); 1 025, 1 250 ($ArOCH_3$); 1 490, 1 590 (Ar); 1 611, 3 175, 3 405 (NH_2); 1 641 ($ArCONH_2$)
XIVd	UV	281 (3·84), 287 (3·84)
	IR	744, 826, 865 (4 and 2 adjacent and solitary Ar–H); 1 025, 1 205, 1 305, 2 855 ($ArOCH_3$); 1 490, 1 563, 1 573, 1 590 (Ar); 1 640 ($ArCONH_2$); 3 180, 3 390 (NH_2)
	^{1}H NMR[a]	3·70 s and 3·80 s, 3 + 3 H (2 OCH_3), 6·50—6·80 m, 3 H (H-3′, H-5′, H-6′); 7·00—7·60 m, 4 H (remaining ArH); 7·85 bs, 2 H (NH_2)
XIVe	UV	infl. 251 (3·84), 307·5 (3·88)
	IR	732, 807, 874 (4 and 2 adjacent and solitary Ar–H); 1 018, 1 037, 1 220, 1 275 ($ArOCH_3$); 1 488, 1 592, 3 000 (Ar); 1 640, 3 350, 3 455 (NH_2); 1 670 ($ArCONH_2$)
	^{1}H NMR[a]	3·62 s and 3·65 s, 3 + 3 H (2 OCH_3); 6·70—7·30 m, 6 H (H-3, H-4, H-5, H-3′, H-4·, H-6′); 7·55 m, 1 H (H-6); 7·40 bs and 7·88 bs, 1 + 1 H (CONH*a*)
XIVf	UV	250 (4·07), infl. 280 (3·93)
	IR	743, 763, 820, 860 (4 and 2 adjacent and solitary Ar–H); 1 228, 1 249 ($ArOCH_3$); 1 500, 1 560, 1 581, 3 040, 3 060 (Ar); 1 606, 1 644, 1 670 ($ArCONH_2$); 3 195, 3 220, 3 280, 3 330, 3 390 (NH_2)
	^{1}H NMR[a]	3·70 s and 3·78 s, 3 + 3 H (2 OCH_3); 6·70—7·35 m, 6 H (H-3, H-4, H-5, H-2′, H-3′, H-6′); 7·50 dd, 1 H (H-6, J = 8·5; 2·5); 7·40 bs and 7·90 bs, 1 + 1 H ($CONH_2$)

TABLE II
(*Continued*)

Compound	Spectrum	Data
XVa	UV	253 (3·98), 287 (3·83)
	IR	749 (4 adjacent Ar–H); 1 255, 1 270, 1 319 ($ArOCH_3$); 1 570, 1 630 (ArCONHR); 1 580, 3 005, 3 080 (Ar); 3 270 (NH)
	^{1}H NMR	2·88 d, 3 H (NCH_3, J = 5·0); 3·72 s, 3 H (OCH_3); 6·60—7·40 m, 7 H (H-3, H-4, H-5, H-3′, H-4′, H-5′, H-6′); 7·60 m, 1 H (H-6)
XVb	UV	251 (3·99), 276 (3·81)
	IR	729, 759, 780, 899 (4 and 2 adjacent and solitary Ar–H); 1 231, 1 285 ($ArOCH_3$); 1 545, 1 640 (ArCONHR); 1 564, 1 573, 1 588, 3 052 (Ar); 3 190 (NH)
	^{1}H NMR	2·90 d, 3 H (NCH_3, J = 5·0); 3·70 s, 3 H (OCH_3); 6·50 bm, 1 H (CONH); 6·65—7·30 m, 7 H (H-3, H-4, H-5, H-2′, H-4′, H-5′, H-6′); 7·50 m, 1 H (H-6)
XVc	UV	228 (4·27), 254 (4·09), infl. 275 (3·90), infl. 300 (3·56)
	IR	744, 833 (4 and 2 adjacent Ar–H); 1 024, 1 225, 1 284 ($ArOCH_3$); 1 492, 1 550, 1 569, 1 589, 3 000, 3 075 (Ar); 1 638 (ArCONHR); 3 295 (NH)
	^{1}H NMR	2·92 d, 3 H (NCH_3, J = 5·0); 3·78 s, 3 H (OCH_3); 6·50 bm, 1 H (NH); 6·70—7·60 m, 8 H (ArH)
XVd	UV	infl. 250 (4·11), 283 (3·87), 289 (3·87)
	IR	750, 840, 860 (4 and 2 adjacent and solitary Ar–H); 1 030, 1 210, 1 310 ($ArOCH_3$); 1 490, 1 590, 3 000, 3 070 (Ar); 1 531, 1 658 (ArCONHR); 3 400 (NH)
	^{1}H NMR	2·92 d, 3 H (NCH_3, J = 5·0); 3·68 s and 3·75 s, 3 + 3 H (2 OCH_3); 6·40 m, 2 H (H-3′, H-5′); 6·80—7·60 m, 6 H (remaining ArH and NH)
XVe	UV	infl. 251 (4·01), 307 (3·92)
	IR	745, 750, 798, 868, 885 (4 and 2 adjacent and solitary Ar–H); 1 018, 1 040, 1 220, 2 275 ($ArOCH_3$); 1 492, 1 590, 3 060 (Ar); 1 548, 1 630 (ArCONHR); 3 300 (NH)
	^{1}H NMR	2·95 d, 3 H (NCH_3, J = 5·0); 3·67 s and 3·69 s, 3 + 3 H (2 OCH_3); 6·84 s, 3 H (H-3′, H-4′, H-6′); 7·10 bq, 1 H (NH); 7·20 m, 3 H (H-3, H-4, H-5); 7·65 m, 1 H (H-6)

XVf	UV	infl. 249 (4·11), infl. 279 (3·93)
	IR	766, 805, 880 (4 and 2 adjacent and solitary Ar–H); 1 230, 1 252, 1 269 ($ArOCH_3$); 1 501, 1 584, 3 000, 3 050, 3 080 (Ar); 1 560, 1 635 (ArCONHR); 3 265 (NH)
	^{1}H NMR	2·95 d, 3 H (NCH_3, J = 5·0); 3·78 s and 3·85 s, 3 + 3 H (2 OCH_3); 6·60 bm, 1 H (NH); 6·75—7·30 m, 6 H (H-3, H-4, H-5, H-2′, H-5′, H-6′); 7·50 m, 1 H (H-6)
XVIa	^{1}H NMR	2·82 s and 3·05 s, 3 + 3 H ($N(CH_3)_2$); 3·79 s, 3 H (OCH_3); 6·70—7·30 m, 8 H (ArH)
XVIb	UV	251 (3·98), 282 (3·79)
	IR	685, 750, 770, 890 (4 and 3 adjacent and solitary Ar–H); 1 046, 1 227 ($ArOCH_3$); 1 570, 1 588, 3 010, 3 060 (Ar); 1 625 ($ArCONR_2$)
	^{1}H NMR	2·80 s and 3·08 s, 3 + 3 H ($N(CH_3)_2$); 3·72 s, 3 H (OCH_3); 6·60—7·30 m, 8 H (ArH)
XVIc	UV	228 (4·24), 251 (4·12), infl. 275 (3·86)
	IR	755, 782, 819, 827 (4 and 2 adjacent Ar–H); 1 026, 1 248 ($ArOCH_3$); 1 491, 1 592, 3 000, 3 050 (Ar); 1 630 ($ArCONR_2$)
XVId	UV	infl. 233 (4·23), infl. 250 (4·12), 293·5 (3·91), 288 (3·91)
	IR	780, 840, 880 (4 and 2 adjacent and solitary Ar–H); 1 030, 1 080, 1 210, 1 305 ($ArOCH_3$); 1 572, 1 580, 1 589, 1 598, 3 010, 3 030, 3 085 (Ar); 1 631 ($ArCONR_2$)
	^{1}H NMR	2·90 s and 3·11 s, 3 + 3 H ($N(CH_3)_2$); 3·71 s and 3·80 s, 3 + 3 H (2 OCH_3); 6·50 m, 2 H (H-3′, H-5′); 6·80—7·50 m, 5 H (remaining ArH)
XVIe	UV	infl. 250 (4·02), 306 (3·86)
	IR	750, 790, 800, 850, 865 (4 and 2 adjacent and solitary Ar–H); 1 048, 1 215, 1 270 ($ArOCH_3$); 1 480, 1 580, 3 000 (Ar); 1 638 ($ArCONR_2$)
	^{1}H NMR	2·86 s and 3·10 s, 3 + 3 H ($N(CH_3)_2$); 3·68 s and 3·75 s, 3 + 3 H (2 OCH_3); 6·80 s, 3 H (H-3′, H-4′, H-6′); 7·25 m, 4 H (remaining ArH)
XVIf	UV	250 (4·17), infl. 280 (3·92)
	IR	765, 775, 835 (4 and 2 adjacent Ar–H); 1 023, 1 228, 1 251 ($ArOCH_3$); 1 500, 1 581, 3 045, 3 075 (Ar); 1 630 ($ArCONR_2$)
	^{1}H NMR	2·82 s and 3·09 s, 3 + 3 H ($N(CH_3)_2$); 3·78 s and 3·83 s, 3 + 3 H (2 OCH_3); 6·70—7·30 m, 7 H (ArH)

TABLE II
(Continued)

Compound	Spectrum	Data
XVIIa	UV	250 (4·02), 284 (3·84)
	IR	750, 778 (4 adjacent Ar–H); 1 020, 1 245, 1 290, 1 315 ($ArOCH_3$); 1 480, 1 505, 1 575, 1 590, 3 060 (Ar); 1 635 ($ArCONR_2$)
	^{1}H NMR	1·08 t, 3 H (CH_3 of ethyl, $J = 7·0$); 1·25 t, 3 H (CH_3 of the second ethyl, $J = 7·0$); 3·18 q and 3·55 q, 2 + 2 H (CH_2NCH_2, $J = 7·0$; 7·0); 3·78 s, 3 H (OCH_3); 6·70–7·40 m, 8 H (ArH)
XIXa	UV	250 (4·04), 284 (3·85)
	IR	755, 775 (4 adjacent Ar–H); 1 025, 1 072, 1 250 ($ArOCH_3$); 1 478, 1 583, 3 060 (Ar); 1 625 ($ArCONR_2$)
	^{1}H NMR	1·14 bdd, 6 H (2 CH_3 of one 2-propyl, $J = 6·0$); 1·58 d, 6 H (2 CH_3 of the second 2-propyl, $J = 6·0$); 3·55 m, 2 H (CHNCH); 3·80 s, 3 H (OCH_3); 6·60–7·40 m, 8 H (ArH)
XIXb	UV	250 (3·97), 280 (3·80)
	IR	679, 739, 755, 790, 870 (4 and 3 adjacent and solitary Ar–H); 1 030, 1 040, 1 232 ($ArOCH_3$); 1 370, 1 375 ($CH(CH_3)_2$); 1475, 1 574, 1 589, 1 593, 3 070 (Ar); 1 630 ($ArCONR_2$)
	^{1}H NMR	1·10 bd, 6 H (2 CH_3 of one 2-propyl); 1·53 d, 6 H (2 CH_3 of the second 2-propyl, $J = 6·0$); 3·50 bm, 2 H (CHNCH); 3·70 s, 3 H (OCH_3); 6·60–7·30 m, 8 H (ArH)
IIb	IR	687, 752, 856 (4 and 3 adjacent and solitary Ar–H); 1 229, 1 247, 1 280 ($ArOCH_3$); 1 574, 1 587 (Ar); 2 758, 2 807 (OCH_3 and NCH_3)
	^{1}H NMR	2·22 s, 6 H ($N(CH_3)_2$); 3·50 s, 2 H ($ArCH_2N$); 3·68 s, 3 H (OCH_3); 6·72 m, 3 H (H-2′, H-4′, H-6′); 7·15 m, 5 H (remaining ArH)
IIc	IR	747, 815, 825 (4 and 2 adjacent Ar–H); 1 025, 1 240 ($ArOCH_3$); 1 486, 1 568, 1 588, 3 005, 3 055 (Ar); 2 751, 2 755, 2 780, 2 800 (NCH_3)
	^{1}H NMR	2·28 s, 6 H ($N(CH_3)_2$); 3·55 s, 2 H ($ArCH_2N$); 3·80 s, 3 H (OCH_3); 6·88 d, 2 H (H-3′, H-5′, $J = 8·5$); 7·10 m, 4 H (H-3, H-4, H-5, H-6); 7·38 d, 2 H (H-2′, H-6′, $J = 8·5$)
IId	IR	760, 825, 879 (4 and 2 adjacent and solitary Ar–H); 1 025, 1 210, 1 255, 1 280 ($ArOCH_3$); 1 490, 1 590, 3 000, 3 050 (Ar); 2 710, 2 760, 2 815 (NCH_3)
	^{1}H NMR	2·25 s, 6 H ($N(CH_3)_2$); 3·55 s, 2 H ($ArCH_2N$); 3·70 s and 3·79 s, 3 + 3 H (2 OCH_3); 6·40 m, 2 H (H-3′, H-5′); 6·70–7·40 m, 5 H (remaining ArH)

IId-HBr	MS	303 (M^+, $C_{17}H_{21}NO_2S$, 7), 227 ($C_{16}H_{11}OS$, 9), 265 ($C_9H_{11}NS$, 100), 164 (58), 150 (C_8H_8NS, 56), 132 (44), 91 (17), 58 (42)
	IR	753, 804, 852 (4 and 2 adjacent and solitary Ar–H); 1 024, 1 165, 1 210 ($ArOCH_3$); 1 570, 1 590, 3 000, 3 050 (Ar); 2 460, 2 620 (NH^+)
IIe	IR[b]	760, 800, 861 (4 and 2 adjacent and solitary Ar–H); 1 020, 1 043, 1 218, 1 270 ($ArOCH_3$); 1 485, 1 587, 3 050 (Ar); 2 770, 2 810, 2 830 ($N–CH_3$)
	^{1}H NMR	2·20 s, 6 H ($N(CH_3)_2$); 3·58 s, 2 H ($ArCH_2N$); 3·58 s and 3·74 s, 3 + 3 H (2 OCH_3); 6·41 d, 1 H (H-6′, J = 2·5); 6·60 dd, 1 H (H-4′, J = 8·5; 2·5); 6·78 d, 1 H (H-3′, J = 8·5); 7·00–7·50 m, 4 H (remaining ArH)
IIIc-HCl	IR	753, 829 (4 and 2 adjacent Ar–H); 1 244 ($ArOCH_3$); 1 497, 1 570, 1 590 (Ar); 2 380, 2 495, 2 685 (NH_2^+); infl. 3 040 (NH)
	^{1}H NMR	2·58 bs, 3 H (NCH_3); 3·79 s, 3 H (OCH_3); 4·30 bs, 2 H ($ArCH_2N$); 6·85 d, 2 H (H-3′, H-5′, J = 8·5); 7·15 m, 3 H (H-3, H-4, H-5); 7·28 d, 2 H (H-2′, H-6′, J = 8·5); 7·78 m, 1 H (H-6); 9·85 bs, 2 H (NH_2^+)
IIId	IR	750, 825, 835, 865 (4 and 2 adjacent and solitary Ar–H); 1 030, 1 209, 1 288, 1 310 ($ArOCH_3$); 1 489, 1 589, 3 000, 3 045 (Ar); 2 790 ($N–CH_3$); 3 275, 3 325, 3 395 (NH)
	^{1}H NMR	1·80 bs, 1 H (NH); 2·40 s, 3 H (NCH_3); 3·74 s and 3·78 s, 3 + 3 H (2 OCH_3); 3·88 s, 2 H ($ArCH_2N$); 6·45 m, 2 H (H-3′, H-5′); 6·80–7·40 m, 5 H (remaining ArH)
IIIe	IR[b]	755, 795, 870 (4 and 2 adjacent and solitary Ar–H); 1 043, 1 220, 1 275 ($ArOCH_3$); 1 485, 1 586, 3 000, 3 055 (Ar); 2 790, 2 835 (OCH_3, NCH_3); 3 320 (NH)
	^{1}H NMR	1·75 s, 1 H (NH); 2·40 s, 3 H (NCH_3); 3·60 s and 3·80 s, 3 + 3 H (2 OCH_3); 3·88 s, 2 H ($ArCH_2N$); 6·39 d, 1 H (H-6′, J = 2·5); 6·65 dd, 1 H (H-4′, J = 8·5; 2·5); 6·82 d, 1 H (H-3′, J = 8·5); 7·10–7·50 m, 4 H (remaining ArH)
IVa	IR	750, 760 (4 adjacent Ar–H); 1 240 ($ArOCH_3$); 1 574, 3 010, 3 050, 3 085 (Ar); 3 300, 3 365, 3 435 (NH_2)
	^{1}H NMR	1·54 s, 2 H (NH_2); 3·90 s, 3 H (OCH_3); 3·98 s, 2 H ($ArCH_2N$); 6·70–7·50 m, 8 H (ArH)
IVc-HCl	IR	760, 800, 845, 885 (4 and 2 adjacent and solitary Ar–H); 1 032, 1 249, 1 290 ($ArOCH_3$); 1 480, 1 491, 1 570, 1 590 (Ar); 2 610, 2 705, 2 730 (NH_3^+); infl. 3 090 (NH_2)

TABLE II
(*Continued*)

Compound	Spectrum	Data
IVd	UV	248 (4·14), 284 (3·87)
	IR[c]	745, 796, 825, 865 (4 and 2 adjacent and solitary Ar–H); 1 210, 1 305 ($ArOCH_3$); 1 485, 1 575, 1 594, 3 000, 3 050 (Ar); 3 315, 3 380, 3 430 (NH_2)
	^{1}H NMR	1·60 s, 2 H (NH_2); 3·80 s, 6 H (2 OCH_3); 3·98 s, 2 H ($ArCH_2N$); 6·45 m, 2 H (H-3′, H-5′); 6·90—7·40, 5 H (remaining ArH)
IVe	IR	765, 805, 860 (4 and 2 adjacent and solitary Ar–H); 1 020, 1 045, 1 060, 1 220, 1 275 ($ArOCH_3$); 1 485, 1 590, 3 000, 3 090 (Ar); 1 620, 3 315, 3 380 (NH_2)
	^{1}H NMR	1·60 bs, 2 H (NH_2); 3·62 s and 3·85 s, 3 + 3 H (2 OCH_3); 3·98 s, 2 H ($ArCH_2N$); 6·32 d, 1 H (H-6′, J = 2·5); 6·65 dd, 1 H (H-4′, J = 8·5; 2·5); 6·80 d, 1 H (H-3′, J = 8·5); 7·10—7·50 m, 4 H (remaining ArH)
IVf	IR	752, 809, 888 (4 and 2 adjacent and solitary Ar–H); 1 024, 1 229, 1 259 ($ArOCH_3$); 1 505, 1 584, 3 000, 3 040 (Ar); 1 610, 3 313, 3 375 (NH_2)
	^{1}H NMR	1·48 bs, 2 H (NH_2); 2·75 s and 2·81 s, 3 + 3 H (2 OCH_3); 3·90 s, 2 H ($ArCH_2N$); 6·60—7·40 m, 7 H (ArH)
Va-HCl	UV	249 (3·94), 284 (3·77)
	IR	750, 784 (4 adjacent Ar–H); 1 020, 1 245, 1 275 ($ArOCH_3$); 1 480, 1 580, 1 592, 3 050, 3 080 (Ar); 2 590, 2 690 (NH^+)
	^{1}H NMR	1·25 t, 6 H (2 CH_3 of ethyls, J = 7·0); 3·1 q, (CH_2NCH_2, J = 7·0); 3·80 s, 3 H (OCH_3); 4·45 s, 2 H ($ArCH_2N$); 6·80—7·50 m and 8·10 m, 8 H (ArH)
Vb	IR[b]	689, 755, 777, 860 (4 and 3 adjacent and solitary Ar-H); 1 042, 1 248 ($ArOCH_3$); 1 479, 1 590, 3 055 (Ar); 2 800 (CH_2–N)
	^{1}H NMR	1·00 t, 6 H (2 CH_3 of ethyls, J = 7·0); 2·50 q, 4 H (CH_2NCH_2, J = 7·0); 3·65 s, 5 H (OCH_3 and $ArCH_2N$); 6·50—7·60 m, 8 H (ArH)

Vc-HCl	MS	301 (M^+, $C_{18}H_{23}NOS$, 30), 286 (20), 272 (40), 229 (100), 227 (80), 197 (20), 193 (50), 184 (10), 178 (20), 86 (30), 72 (15), 70 (20)
	IR	759, 850 (4 and 2 adjacent Ar–H); 1 020, 1 244 ($ArOCH_3$); 1 487, 1 570, 1 588, 3 065 (Ar); 2 375 (NH^+)
	^{1}H NMR[a,d,e]	1·31 t, 6 H (2 CH_3 of ethyls, J = 7·0); 3·18 q, 4 H (CH_2NCH_2, J = 7·0); 3·81 s, 3 H (OCH_3); 4·48 s, 2 H ($ArCH_2N$); 7·02 d, 2 H (H-3′, H-5′, J = 8·5); 7·20—7·50 m and 8·10 m, 5 + 1 H (remaining ArH)
VIa-HCl	UV	249 (4·06), 271 (3·90), 287 (3·86)
	IR	755,780 (4 adjacent Ar–H); 1 020, 1 245, 1 275 ($ArOCH_3$); 1 479, 1 580, 1 590, 3 050, 3 080 (Ar); 2 520 (NH^+)
	^{1}H NMR[a]	0·90 t, 6 H (2 CH_3 of propyls, J = 7·0); 1·80 bm, 4 H (2 CH_2 in positions 2 and 2′ of propyls); 3·00 bm, 4 H (CH_2NCH_2); 3·88 s, 3 H (OCH_3); 4·55 s, 2 H ($ArCH_2N$); 6·80—7·60 m and 8·20 m, 7 + 1 H (ArH)
VIb	^{1}H NMR	0·80 t, 6 H (2 CH_3 of propyls); 1·40 m, 4 H (2 CH_2 in positions 2 and 2′ of propyls); 2·31 t, 4 H (CH_2NCH_2); 3·64 s, 2 H ($ArCH_2N$); 3·70 s, 3 H (OCH_3); 6·50—7·70 m, 8 H (ArH)
VIc	UV	228 (4·36), 245 (4·34), infl. 268 (3·99), 290 (3·90)
	IR	750, 847 (4 and 2 adjacent Ar–H); 1 245 ($ArOCH_3$); 1 500, 1 568, 1 587, 3 015, 3 090 (Ar); 2 260 (NH^+)
	^{1}H NMR[a,e]	0·88 t, 6 H (2 CH_3 of propyls); 1·85 m, 4 H (2 CH_2 in positions 2 and 2′ of propyls); 3·00 m, 4 H (CH_2NCH_2 of dipropylamino), 3·84 s, 3 H (OCH_3); 4·51 bd, 2 H ($ArCH_2N$); 7·08 d, 2 H (H-3′, H-5′, J = 9·0); 7·15—7·60 m, 5 H (H-3, H-4, H-5, H-2′, H-6′); 8·12 m, 1 H (H-6)
VIIa-HCl	UV	247 (3·96), 286 (3·76)
	IR	745, 762 (4 adjacent Ar–H); 1 015, 1 040, 1 248, 1 272 ($ArOCH_3$); 1 475, 1 582, 3 050, 3 060 (Ar), 2 510, 2 555, 2 590, 2 620 (NH^+)
	^{1}H NMR[a]	1·45 d and 1·54 d, 12 H (4 CH_3 of 2-propyls); 3·80 bm, 2 H (CHNCH); 3·88 s, 3 H (OCH_3); 4·55 s, 2 H ($ArCH_2N$); 6·90—7·60 m and 8·30 m, 7 + 1 H (ArH)
VIIb	^{1}H NMR	0·90 d, 12 H (4 CH_3 of 2-propyls); 2·95 m, 2 H (CHNCH); 3·69 s, 5 H (OCH_3 and $ArCH_2N$); 6·50—7·80 m, 8 H (ArH)
VIIc-HCl	MS	329 (M^+, $C_{20}H_{27}NOS$, 20), 314 (50), 286 (10), 229 (100), 227 (80), 221 (10), 214 (20), 213 (10)
	UV	246 (4·17)
	IR	755, 826, 854 (4 and 2 adjacent Ar–H); 1 034, 1 250 (OCH_3); 1 500, 1 593, 3 040 (Ar); 2 503 (NH^+)
	^{1}H NMR[a,e]	1·42 d and 1·50 d, 12 H (4 CH_3 of 2-propyls, J = 6·5); 3·78 bm, 2 H (CHNCH); 3·81 s, 3 H (OCH_3); 4·52 bd, 2 H ($ArCH_2N$); 7·06 d, 2 H (H-3′, H-5′, J = 9·0); 7·10—7·60 m, 5 H (H-3, H-4, H-5, H-2′, H-6′); 8·30 m, 1 H (H-6)

TABLE II
(*Continued*)

Compound	Spectrum	Data
XXIa	UV	249 (3·90), 287 (3·76)
	IR	758 (4 adjacent Ar–H); 1 205, 1 250, 1 300 (ArOH); 1 558, 1 588, 3 005, 3 050 (Ar); 2 515, 2 620 (NH^+)
	^{1}H NMR	2·35 s, 6 H ($N(CH_3)_2$); 3·62 s, 2 H ($ArCH_2N$). 6·60–7·70 m, 8 H (ArH)
XXIb	UV	250 (3·99), 280 (3·76), 287 (3·76), infl. 294 (3·70)
	IR	685, 755, 770, 840, 895 (4 and 3 adjacent and solitary Ar–H); 1 262 (ArOH); 1 580, 3 045 (Ar); 2 580 (NH^+)
	^{1}H NMR	2·15 s, 6 H ($N(CH_3)_2$); 3·60 s, 2 H ($ArCH_2N$); 6·25–6·80 m, 3 H (H-2′, H-4′, H-6′); 6·90–7·50 m, 5 H (remaining ArH); 9·05 bs, 1 H (OH)
XXIb-HM[f]	MS	259 (M^+, $C_{15}H_{17}NOS$, 79), 244 (55), 213 (74), 197 (14), 184 (9), 165 (23), 152 (12), 137 (18), 132 (45), 121 (16), 91 (23), 58 (100), 44 (31), 28 (90)
XXIc	UV	231 (4·17), 274 (4·19), infl. 280 (3·82)
	IR	750, 829 (4 and 2 adjacent Ar–H); 1 240, 1 270 (ArOH); 1 492, 1 582, 1 587, 1 596, 3 045 (Ar); 2 465, 2 505, 2 640 (NH^+)
	^{1}H NMR	2·35 s, 6 H ($N(CH_3)_2$); 3·58 s, 2 H ($ArCH_2N$); 6·63 d, 2 H (H-3′, H-5′, $J = 8·5$); 6·80–7·40 m, 4 H (H-3, H-4, H-5, H-6); 7·19 d, 2 H (H-2′, H-6′, $J = 8·5$); 8·75 s, 1 H (OH)
XXId	MS	275 (M^+, $C_{15}H_{17}NO_2S$, 36), 260 ($C_{14}H_{14}NO_2S$, 7); 229 ($C_{13}H_{11}O_2S$, 18), 165 ($C_9H_{11}NS$, 60); 164 (50), 150 (34), 132 ($C_9H_{10}N$, 42), 91 (30), 58 (100), 44 (42), 42 (49)
	UV	245 (4·04), 290 (3·76)
	IR	760, 785, 860 (4 and 2 adjacent Ar–H); 1 195, 1 254 (ArOH); 1 560, 3 050 (Ar); 2 480, 2 580 (NH^+); 3 220 (OH)
	^{1}H NMR[a]	2·16 s, 6 H ($N(CH_3)_2$); 3·50 s, 2 H ($ArCH_2N$); 6·20 m, 2 H (H-3′, H-5′); 6·80–7·30 m, 5 H (remaining ArH)

XXIe	UV	infl. 235 (3·98), 312 (3·71)
	IR	755, 760, 795, 812, 835, 875 (4 and 2 adjacent and solitary Ar–H); 1 210, 1 255 (ArOH); 1 565, 1 600 (Ar); 2 650, 2 720 (NH^+); 3 460 (OH)
	^{1}H NMR[a]	2·14 s, 6 H ($N(CH_3)_2$); 3·48 s, 2 H ($ArCH_2N$); 6·55 s, 3 H (H-3′, H-4′, H-6′); 7·18 m, 4 H (remaining ArH); 9·20 bs, 1 H (OH)
XXIf	UV	248·5 (4·11), 287 (3·81)
	IR	755, 820, 855 (4 and 2 adjacent and solitary Ar–H); 1 255 (ArOH); 1 590, 3 050 (Ar); infl. 2 500 (NH^+); 3 365 (OH)
	^{1}H NMR[a]	2·20 s, 6 H ($N(CH_3)_2$); 3·50 s, 2 H ($ArCH_2N$); 6·70—7·50 bm, 7 H (ArH)
XXIIa	UV	247 (3·87), 287 (3·76)
	IR	760, 766 (4 adjacent Ar–H); 1 248 (ArOH); 1 565, 3 020, 3 040, 3 070 (Ar); 2 380 (NH^+)
	^{1}H NMR	2·42 s, 3 H (NCH_3); 3·90 s, 2 H ($ArCH_2N$); 7·00 s, 1 H (OH); 6·60—7·70 m, 8 H (ArH)
XXIIb	UV	248 (3·96), 277 (3·73), 286 (3·75)
	IR	757, 780, 893 (4 and 2 adjacent and solitary Ar–H); 1 156 (ArOH); 1 575, 1 593 (Ar); 3 260 (OH, NH)
	^{1}H NMR[a]	2·25 s, 3 H (NCH_3); 3·71 s, 2 H ($ArCH_2N$); 5·10 flat s, 2 H (OH and NH); 6·50—7·60 m, 8 H (ArH)
XXIIc	UV	infl. 230 (4·11), 248 (4·15), infl. 276 (3·81)
	IR[c]	755, 830, 849 (4 and 2 adjacent Ar–H); 1 240, 1 279 (ArOH); 1 572, 1 593, 3 053, 3 070 (Ar); 2 470, 2 550, 2 640 (NH_2^+); 3 275, 3 420 (OH, NH)
	^{1}H NMR	2·40 s, 3 H (NCH_3); 3·88 s, 2 H ($ArCH_2N$); 5·98 bs, 2 H (NH and OH); 6·60 d, 2 H (H-3′, H-5′); 7·15 m, 6 H (remaining ArH)
XXIId	IR	750, 770, 800, 849, 871 (4 and 2 adjacent and solitary Ar–H); 1 110, 1 140, 1 190, 1 230, 1 255 (ArOH); 1 570, 3 040 (Ar); 2 400 (NH_2^+); 3 420 (OH, NH)
	^{1}H NMR[a]	2·35 s, 3 H (NCH_3); 3·81 s, 2 H ($ArCH_2N$); 6·25 m, 2 H (H-3′, H-5′); 6·60 bs, 3 H (2 OH and NH); 6·90—7·40 m, 5 H (remaining ArH)
XXIIe	UV	infl. 242·5 (3·74), 311 (3·54)
	IR	750, 812, 858 (4 and 2 adjacent and solitary Ar–H); 1 160, 1 215 (ArOH); 1 570, 1 600 (Ar); 2 380, 2 480, 2 660 (NH_2^+)
	^{1}H NMR[a]	2·23 s, 3 H (NCH_3); 3·75 s, 2 H ($ArCH_2N$); 6·20 bs, 3 H (2 OH and NH); 6·50 m, 3 H (H-3′, H-4′, H-6′); 7·25 m, 4 H (remaining ArH)

TABLE II
(*Continued*)

Compound	Spectrum	Data
XXIIf	UV	248 (4·11), 287 (3·81)
	IR	753, 809, 860 (4 and 2 adjacent and solitary Ar–H); 1 260 (ArOH); 1 587, 3 050 (Ar); 2 600 (NH_2^+); infl. 3 150, 3 290 (OH and NH)
	^{1}H NMR[a]	2·05 bs, 3 H (NCH_3); 3·50 bs, 2 H ($ArCH_2N$); 5·40 bs, 3 H (2 OH and NH); 6·40—7·20 bm, 7 H (ArH
XXIIIa	UV	247 (3·98), 286 (3·78)
	IR	750, 759, 767 (4 adjacent Ar–H); 1 120, 1 148 (ArOH); 1 543, 1 580 (Ar); 2 330, 2 410, 2 580 (NH_3^+); 3 140, 3 280, 3 335 (OH, NH_2)
	^{1}H NMR[a]	3·82 s, 2 H ($ArCH_2N$); 5·20 bs, 3 H (OH and NH_2); 6·50—7·50 m, 8 H (ArH)
XXIIIb	UV	248 (4·00), infl. 279 (3·70); 285 (3·72); 294 (3·65)
	IR	690, 749, 780, 864, 892 (4 and 3 adjacent and solitary Ar–H); 1 232, 1 279 (ArOH); 1 500, 1 571, 1 590, 3 050 (Ar); 1 640 (NH_2); 2 560, 2 630 (NH_3^+); 3 220, 3 295, 3 335, 3 365, 3 400 (OH and NH_2)
	^{1}H NMR	3·80 bs, 2 H ($ArCH_2N$); 4·50 bs, 2 H (NH_2); 6·60 m, 2 H (H-2′, H-4′); 6·90—7·70 m, 6 H (remaining ArH)
XXIIIc	UV	248 (4·01), infl. 285 (3·69)
	IR	739, 830 (4 and 2 adjacent Ar–H); 1 252, 1 276 (ArOH); 1 490, 1 578, 3 050 (Ar); 2 550, 2 645 (NH^+); 3 290, 3 345 (OH and NH_2)
	^{1}H NMR[a]	3·75 s, 2 H ($ArCH_2N$); 4·30, bs, 3 H (OH and NH_2); 6·80 d, 2 H (H-3′, H-5′, J = 9·0); 7·20 d, 2 H (H-2′, H-6′, J = 9·0); 6·70—7·50 m, 4 H (remaining ArH)
XXIIIe	UV	241 (3·80), 311 (3·59)
	IR	760, 765, 776, 822, 830, 860, 872 (4 and 2 adjacent and solitary Ar–H); 1 192, 1 205 (ArOH); 1 475, 1 580, 1 604 (Ar); 2 520 (NH_3^+); 2 290, 2 350, 3 415 (OH, NH_2)
	^{1}H NMR[a]	3·75 s, 2 H ($ArCH_2N$); 5·20 bs, 4 H (2 OH and NH_2); 6·20—6·70 m, 3 H (H-3′, H-4′, H-6′); 7·25 m, 4 H (remaining ArH)

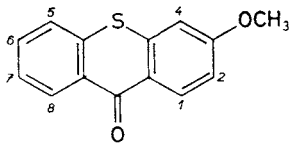
XXIIIf	UV	250 (4·11), 287 (3·82)
	IR	755, 813, 871 (4 and 2 adjacent and solitary Ar–H); 1 210 (ArOH); 1 492, 1 589 (Ar); 2 560 (NH_3^+); 3 180, 3 280, 3 340 (OH, NH_2)
	^{1}H NMR[a]	3·80 bs, 2 H ($ArCH_2N$); 5·25 bs, 4 H (2 OH and NH_2); 6·50—7·50 bm, 7 H (ArH)
XXIV-HCl	UV	250 (4·20), 270 (4·14), 286 (4·11)
	IR[d]	754, 780 (4 adjacent Ar–H); 1 293, 1 350 (ArOH); 1 472, 1 494, 1 585 (Ar); 2 490, 2 560, 2 645, 2 715 (NH^+); 3 430 (OH)
	^{1}H NMR[a]	1·35 t, 6 H (2 CH_3 of ethyls, J = 7·0); 3·20 q, 4 H (CH_2NCH_2 of diethylamino, J = 7·0); 4·54 s, 2 H ($ArCH_2N$); 6·70—7·50 m and 8·05 m, 7 + 1 H (ArH)
XXIVb-HCl	MS	287 (M^+, $C_{17}H_{21}NOS$, 40), 272 (50), 258 (30), 215 (90), 213 (100)
	UV	245 (4·22), 271 (3·98), 284 (3·95), 294 (3·90)
	IR	700, 753, 805, 882, 894 (4 and 2 adjacent and solitary Ar–H); 1 215, 1 300 (ArOH); 1 581 (Ar); 2 755 (NH^+); 3 155 (OH)
	^{1}H NMR[a,d,e]	1·31 t, 6 H (2 CH_3 of ethyls, J = 7·0); 3·18 q, 4 H (CH_2NCH_2 of diethylamino, J = 7·0); 4·48 s, 2 H ($ArCH_2N$); 6·80—7·60 m and 8·15 m, 7 + 1 H (ArH)
XXIVc-HCl	UV	246 (4·41), infl. 268 (4·27), infl. 292 (4·05)
	IR	750, 848 (4 and 2 adjacent Ar–H); 1 217, 1 280 (ArOH); 1 490, 1 572, 1 595 (Ar); 2 625 (NH^+); 3 040 (OH)
	^{1}H NMR[a,e]	1·35 t, 6 H (2 CH_3 of ethyls, J = 7·0); 3·20 bq, 4 H (CH_2NCH_2 of diethylamino); 4·48 bd, 2 H (H-3′, H-5′, J = 9·0); 7·10—7·60 m, 5 H (H-3, H-4, H-5, H-2′, H-6′); 8·10 m, 1 H (H-6)
XXVa-HCl	UV	249 (3·87), 286 (3·76)
	IR	752, 770 (4 adjacent Ar–H); 1 295, 1 350 (ArOH); 1 490, 1 584 (Ar); 2 520, 2 553, 2 605 (NH^+); infl. 3 060 (OH)
	HNMR[a,g]	0·85 t, 6 H (2 CH_3 of propyls, J = 7·0); 1·75 m, 4 H (2 CH_2 in positions 2 and 2′ of propyls); 3·00 m, 4 H (CH_2NCH_2 of dipropylamino); 4·45 s, 2 H ($ArCH_2N$); 6·60—7·40 m and 7·98 m, 7 + 1 H (ArH)
XXVb-HCl	UV	244 (4·00), 284 (3·72)
	IR	710, 751, 760, 800, 890 (4 and 3 adjacent and solitary Ar–H); 1 220, 1 250 (ArOH); 1 486, 1 586 (Ar); 2 518, 2580 (NH^+); 3 125 (OH)
	^{1}H NMR[a,e]	0·85 t, 6 H (2 CH_3 of propyls); 1·80 bm, 4 H (2 CH_2 in positions 2 and 2′ of propyls); 2·98 bm, 4 H (CH_2NCH_2 of dipropylamino); 4·50 bd, 2 H ($ArCH_2N$); 6·60—7·60 m, 7 H (H-3, H-5, H-4, H-2′, H-4′, H-5′, H-6′); 8·12 m, 1 H (H-6)

TABLE II
(*Continued*)

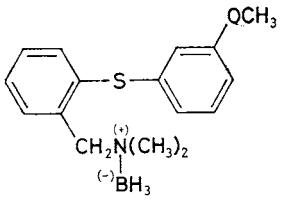
Compound	Spectrum	Data
XXVc-HCl	UV	246 (4·37), infl. 269 (4·21), infl. 292 (3·98)
	IR	754, 840 (4 and 2 adjacent Ar–H); 1 277 (ArOH); 1 493, 1 579, 1 595 (Ar); 2 525, 2 625, 2 700 (NH^+); 3 100 (OH)
	^{1}H NMR[a,e]	0·90 t, 6 H (2 CH_3 of propyls); 1·85 m, 4 H (2 CH_2 in positions 2 and 2′ of propyls); 3·05, 4 H (CH_2NCH_2 of dipropylamino); 4·51 s, 2 H ($ArCH_2N$); 6·95 d, 2 H (H-3′, H-5′, J = 9·0); 7·10—7·50 m, 5 H (H-3, H-4, H-5, H-2′, H-6′); 8·10 m, 1 H (H-6)
XXVIa	MS	315 (M^+, $C_{19}H_{25}NOS$, 14), 300 (26), 287 (1), 273 (7), 272 (3), 230 (5), 215 (78), 213 (100), 197 (7), 185 (10), 181 (10), 91 (32), 86 (22)
XXVIa-HCl	UV	247 (3·92), 283 (3·81)
	IR	749, 753 (4 adjacent Ar–H); 1 117, 1 170 (ArOH); 1 480, 1 582 (Ar); 2 510, 2 555, 2 650, 2 680 (NH^+); 3 070 (OH)
	^{1}H NMR[a,e]	1·40 d and 1·49 d, 6 + 6 H (4 CH_3 of 2-propyls, J = 6·5); 3·80 m, 2H CHNCH); 4·55 bd, 2 H ($ArCH_2N$); 6·80—7·50 m, 7 H (H-3, H-4, H-5, H-3′, H-4′, H-5′, H-6′); 8·08 m, 1 H (H-6)
XXVIb-HBr	MS	315 (M^+,$C_{19}H_{25}NOS$, 9), 300 (37), 272 (1·5), 215 (73), 213 (100), 197 (6), 185 (7), 181 (8), 91 (12), 86 (11)
XXVIb-HCl	UV	infl. 245 (4·12), infl. 269 (3·94), 284 (3·86), infl. 290 (3·85)
	IR	690, 755, 790, 892 (4 and 3 adjacent and solitary Ar–H); 1 221 (ArOH); 1 480, 1 575, 1 585, 1 593, 1 605 (Ar); 2 665 (NH^+); 3 100 (OH)
	^{1}H NMR[a,e]	1·36 d and 1·45 d, 12 H (4 CH_3 of 2-propyls, J = 6·5); 3·80 bm, 2 H (CHNCH); 4·52 bd, 2 H ($ArCH_2N$); 6·60—8·20 m, 8 H (ArH)
XXVIc-HCl	UV	246 (4·22)
	IR	750, 843 (4 and 2 adjacent Ar–H); 1 230, 1 268 (ArOH); 1 497, 1 576, 1 594 (Ar); 2 645 (NH^+); 3 055 (OH)
	^{1}H NMR[a,e]	1·41 d and 1·49 d, 12 H (4 CH_3 of 2-propyls, J = 6·5); 3·80 bm, 2 H (CHNCH); 4·51 bd, 2 H ($ArCH_2N$); 6·95 d, 2 H (H-3′, H-5′, J = 9·0); 7·10—7·60 m, 5 H (H-3, H-4, H-5, H-3′, H-5′); 8·10 m, 1 H (H-6)

[a] In CD_3SOCD_3; [b] film; [c] in KBr; [d] at 80°C; [e] 100 MHz; [f] HM hydrogen maleate; [g] at 120°C.

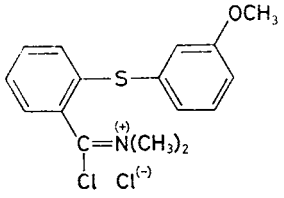
to crystalline salts and spectra were recorded either with these salts or with the homogeneous bases. The amine *IIb* proved an important intermediate and, therefore, its preparation was investigated more carefully. It was first found that it is possible to reduce *XVIb* with diborane (for the method, cf. ref.[17]) generated "in situ" by reaction of sodium borohydride with boron trifluoride etherate in tetrahydrofuran (ref.[18]). The primary product, which was isolated as a crystalline solid after mild acid hydrolysis of the reaction mixture, was identified as the amine borane *XXXIII*. A similar product was isolated by us[19] in an attempt to reduce an enamine by the same reducing agent. Hydrolysis of *XXXIII* with sodium hydroxide in boiling aqueous ethanol gave smoothly the desired *IIb* and when the step of hydrolysis was inserted into the whole procedure, there resulted an advantageous process for preparing *IIb* from *XVIb* in a satisfactory yield. Another possibility was found in the reaction of *XVIb* with phosphoryl chloride, followed by sodium borohydride in ethanol (for the method, cf. ref.[20]). The reaction proceeds probably via the Vilsmeier complex *XXXIV* (ref.[21]), which is reduced. The desired *IIb* was obtained in the form of hydrochloride in a rather low yield. Two minor by-products were isolated from the neutral fraction. The first of them was identified as the already mentioned 3-methoxythioxanthone (*XXXII*) being probably formed by cyclization of the amide *XVIb* with phosphoryl chloride (another case of cyclization of a tertiary amide to a tricyclic ketone was observed some time ago[22]). The second by-product, being $C_{14}H_{12}$. .OS (analysis and mass spectrum), is assumed to be *XXXV* which is in good agreement with its spectra. Such a compound could have been formed either by direct reduction of *XXXII* or via the corresponding 9-hydroxy compound and by its disproportionation (cf. ref.[23]). Another possibility for preparing *IIb* is the Leuckart reaction[24] of *XIIb* with dimethylformamide and formic acid at 180°C (cf. ref.[25]).



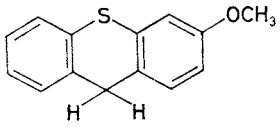
XXXII



XXXIII



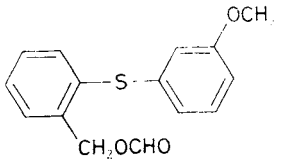
XXXIV



XXXV

The amine *IIb* was obtained in the form of hydrochloride in the yield of 75%. By chromatography of the neutral fraction, three minor by-products were separated. The less polar seems to correspond surprisingly to the compound considered to be *XXXV* (melting point and comparison by TLC). The other is oily and its mass spectrum estimates its elemental composition as $C_{15}H_{14}O_3S$. The ^1H and ^{13}C NMR spectra identify the compound to be the formic ester *XXXVI*. The third one is again 3-methoxythioxanthone (*XXXII*) whose formation here is rather obscure (similarly like that of *XXXV*).

The amine *IId* was prepared by method *D-1* but in addition also from the aldehyde *XIId* in three steps: *XIId* was reduced with sodium borohydride in aqueous ethanol to 2-(2,4-dimethoxyphenylthio)benzyl alcohol which was transformed by treatment with thionyl chloride in boiling benzene to 2-(2,4-dimethoxyphenylthio)benzyl chloride. Its reaction with dimethylamine in chloroform in autoclave at 75°C gave *IId* which was transformed to the picrate (described in Experimental). Both of the intermediates were crystalline but were processed without characterization.

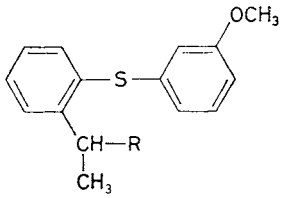


XXXVI

The methoxylated amines were demethylated to the phenolic amines *XXIa* to *XXIIIf* and *XXIVa–XXVIc* using two general methods: (i) heating with pyridine hydrochloride to 210–220°C (bath temperature) (method *E*) and (ii) treatment with boron tribromide in chloroform at room temperature (method *F*). The most important amine *XXIb* was prepared by two further methods (see Experimental). The first consisted in demethylation of *IIb* with concentrated hydrobromic acid at 120°C. The second method was an attempt to carry out the synthesis of *XXIb* without protecting the phenolic hydroxyl by O-methylation, which was successful, in principle. 3-Hydroxythiophenol[26] was refluxed with 2-iodobenzoic acid in aqueous potassium hydroxide in the presence of copper and gave *XXXb* in a reasonable yield (the spectra corroborated the structure). The following reaction with dimethylamine, leading to *XXXIb*, was carried out in the presence of the complex of triphenylphosphine and tetrachloromethane in tetrahydrofuran (for the method, cf. ref.[27]); the desired *XXXIb* was obtained by chromatography of the crude product. This method was found more favourable than that using titanium tetrachloride in tetrahydrofuran[28]. Reduction of *XXXIb* with lithium aluminium hydride in tetrahydrofuran gave *XXIb* in a high yield. The phenolic bases *XXIa–XXIIIf* were crystalline; amines *XXIVa–XXVIc* (with the exception of *XXVIa*) were oily. All

the bases were transformed to crystalline salts and the spectra were recorded either with the crystalline bases or hydrochlorides.

For introducing a chiral centre into the molecule of *XXIb*, the α-methyl homologue *XXVIIb* was synthesized. The aldehyde *XIIb* was reacted with methylmagnesium iodide in a mixture of ether and benzene and the obtained secondary alcohol *XXXVII* was treated with thionyl chloride in boiling benzene in the presence of a small amount of dimethylformamide to give the chloride *XXXVIII* whose reaction with dimethylamine in dioxane in the autoclave at 90°C gave *VIIIb*. Even under these conditions, more than 30% of the starting *XXXVIII* were recovered indicating a rather low reactivity of this benzylic chloro compound, probably due to steric hindrance. Demethylation of *VIIIb* with boiling hydrobromic acid afforded the crystalline racemic *XXVIIb*, obtained via the hydrobromide. Attempts to resolve *XXVIIb* by means of L(−)-malic acid were unsuccessful: the salt on crystallization remains diastereomeric mixture. It was necessary to resolve the precursor *VIIIb* which proceeded in the form of salts with (−)-O,O′-dibenzoyl-L-tartaric and (+)-O,O′-dibenzoyl-D-tartaric acids. The obtained homogeneous diastereoisomeric salts were decomposed with aqueous ammonia and the crude optically active bases *VIIIb* were directly demethylated with boiling hydrobromic acid. The resulting crystalline (+)-hydrobromide and (−)-hydrobromide gave by treatment with aqueous ammonia (−)-*XXVIIb* and (+)-*XXVIIb*, respectively.

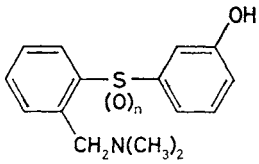


XXXVII, R = OH
XXXVIII, R = Cl

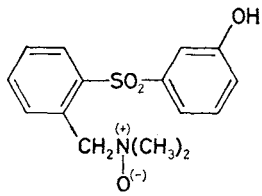
Reaction of *XIIIb* with 2-dimethylaminoethylamine in benzene at 10−20°C gave the oily amide *XXb* which was reduced without characterization with diborane "in situ" in tetrahydrofuran to *IXb* (crystalline dihydrochloride and ^{1}H NMR spectrum). This amine was methylated with formic acid and aqueous formaldehyde at 100°C (Eschweiler–Clarke method[24]) to *Xb* (dihydrochloride and spectra). The methoxy amines *IXb* and *Xb* were demethylated by boiling hydrobromic acid to *XXVIIIb* and *XXIXb* (structures confirmed by ^{1}H NMR spectra).

Oxidation of *XXIb* with hydrogen peroxide in acetic acid at room temperature (reaction time of 12 h) gave the sulfoxide *XXXIX*. Similar oxidation with a larger excess of hydrogen peroxide and longer reaction time (3−7 days) resulted in the formation of the sulfone *XL*, accompanied eventually by the sulfone N-oxide *XLI*,

separated on the basis of different solubility. Oxygen functions in these oxidation products were characterized by IR spectra and the overall structures were confirmed by ^{1}H NMR spectra.



XXXIX, n = 1
XL, n = 2



XLI

The compounds described in this communication were pharmacologically tested in the form of salts, described in the Experimental and in Table I. On the basis of preliminary findings, a part of the compounds was tested as potential antidepressants. In this line, they were administered orally and the doses given were calculated per bases. Table III assembles the code numbers of the compounds tested, their acute toxicities in mice (LD_{50}), and the IC_{50} values characterizing the affinities of the compounds to the binding sites of imipramine and desipramine in hypothalamus of the rat brain and the influence on re-uptake of 5-hydroxytryptamine in rat brain and of noradrenaline in the rat brain cortex.

The data in Table III were supplemented by some findings in animal tests, especially in the line of antireserpine activities: (i) Inhibition of reserpine-induced ptosis in mice, ED (significant effect) in mg/kg (in parentheses the threshold doses): *IIIa*, 25; *IIIb*, 25; *IIIc*, 25 (10); *IIIf*, 25 (3); *XXIa*, 25 (10); *XXIb*, 25 (3); *XXIc*, 25 (10); *XXId*, 25 (10); *XXIe*, 25; *XXIf*, 25; *XXIIa*, >25; *XXIIb*, 25; *XXIIc*, 12·5; *XXIId*, >25; *XXIIe*, >25; *XXIIf*, 6·25; *XXIIIa*, >25; *XXIIIb*, >25; *XXIIIc*, >25; *XXIIIf*, >25; *XXIVb*, >25; *XXIVc*, >25; *XXVa*, >25; *XXVb*, >25; *XXVc*, >300; *XXVIa*, >25; *XXVIb*, >300; *XXVIc*, >25; (±)-*XXVIIb*, 100 (30); (+)-*XXVIIb*, 100 (30); (−)-*XXVIIb*, 100. (ii) Antagonization of reserpine hypothermia in mice, ED (significant effect) in mg kg: *IIIb*, >10; *IIIc* and *IIIf* antagonize the hypothermia in doses of 10–100 mg/kg without relation of effect to the dose; *XXIb*, 10; *XXIc*, >10; *XXId*, >10; *XXIf*, 10; *XXIIb*, >10; *XXIIc*, >10; *XXIIf*, 10; *XXIIIb*, >10. (iii) Antagonization of the ulcerogenic effect of reserpine in rats, ED (significant effect) in mg/kg: *IIIa*, >50; *IIIb*, 50; *IIIc*, 50; *IIIf*, 50; *XXIa*, 50; *XXIb*, 50 (in the dose of 50 mg/kg it also inhibits the formation of the indomethacin-induced gastric ulcers in rats); *XXIc*, 50; *XXId*, >50; *XXIf*, 50; *XXIIf*, >50; *XXIIIf*, >50.

[a] Acute toxicity in mice on oral administration. [b] Inhibition of binding of 4 nM [^{3}H]imipramine in hypothalamus of the rat brain. [c] Inhibition of binding of 4 nM [^{3}H]desipramine in hypothalamus of the rat brain. [d] Inhibition of re-uptake of 10 nM [^{3}H]5-hydroxytryptamine in the rat brain. [e] Inhibition of re-uptake of 10 nM [^{3}H]noradrenaline in the cortex of rat brain. [f] Not estimated. [g] LD_{100} orally.

TABLE III

Acute toxicity and biochemical pharmacology of some 2-(methoxy- and -hydroxy-phenylthio)-benzylamine including standards

Compound	Code number VÚFB-	LD_{50}[a] mg/kg	IC_{50} in nM			
			IMI[b]	DES[c]	5HT[d]	NA[e]
IIIa	15 430	148	34·3	49	24·2	8·2
IIIb	15 431	301	29·5	293	11·8	7·0
IIIc	15 432	189	6·7	2 906	8·9	2 405
IIIf	15 433	153	12·2	807·1	151·7	11 840
XXIa	15 467	467	191·3	1 339	—[f]	—[f]
XXIb	15 468	217	3·3	2 185	0·6	18 812
XXIc	15 469	209	8·2	13·8	2·5	9·4
XXId	15 596	210	39·6	1 198	183·9	1 294
XXIf	15 470	306	<100	>100	4·1	1 425
XXIIa	15 427	458	<100	>100	—[f]	—[f]
XXIIb	15 428	343	17·7	>100	—[f]	—[f]
XXIIc	15 429	162	<100	—[f]	—[f]	—[f]
XXIId	15 531	448	>100	>100	—[f]	—[f]
XXIIe	15 529	423	>100	>100	—[f]	—[f]
XXIIf	15 466	630	>100	>100	—[f]	—[f]
XXIIIa	15 424	>500	>100	>100	—[f]	—[f]
XXIIIb	15 425	c. 500	<500	>100	—[f]	—[f]
XXIIIc	15 426	338	>500	>100	—[f]	—[f]
XXIIIe	15 528	598	>100	>100	—[f]	—[f]
XXIIIf	15 465	665	>100	>100	—[f]	—[f]
XXIVb	17 142	222	>100	>100	>100	>100
XXIVc	17 144	404	>100	>100	>100	>100
XXVa	17 112	>2 000	>100	>100	>100	>100
XXVb	17 140	1 379	>100	>100	>100	>100
XXVc	17 164	—[f]	>100	>100	—[f]	—[f]
XXVIa	17 141	1 146	>100	>100	>100	>100
XXVIb	17 163	—[f]	>100	>100	—[f]	—[f]
XXVIc	17 143	704	>100	>100	>100	>100
(±)-*XXVIIb*	17 658	500[g]	—[f]	—[f]	72·5	4 411
(+)-*XXVIIb*	17 659	500[g]	—[f]	—[f]	19·7	151
(−)-*XXVIIb*	17 660	500[g]	—[f]	—[f]	12·4	6 606
XXXIX	17 655	500[g]	—[f]	—[f]	680·5	6 910
XL	17 656	500[g]	—[f]	—[f]	405·7	41 023
XLI	17 657	500[g]	—[f]	—[f]	19 171	29 673
Citalopram			29·2	3 183	0·4	13 718
Amitriptyline			20·2	411·7		
Nortriptyline			391·8	13·3		
Imipramine			10·9	40·0		
Desipramine			317·5	2·0		
Dosulepin			36·4	298·7		

On the basis of data given in Table III and in the last paragraph, it may be concluded that some of the methoxylated secondary amines (*IIIc*, *IIIf*) and especially some of the hydroxylated tertiary amines (*XXIb*, *XXIc*, *XXId*, *XXIf*) are highly active and selective inhibitors of 5-hydroxytryptamine re-uptake in the brain structures and are active in the antireserpine tests. The most interesting compound of the series is *XXIb* (hydrogen maleate VÚFB-15 468) showing a higher degree of selectivity of inhibition of 5-hydroxytryptamine re-uptake than the known citalopram[29] and is undergoing preclinical studies. The stereoselectivity of action of enantiomers of *XXVIIb* was shown only in the test of inhibition of re-uptake of 10 nm [^{3}H]-noradrenaline in the cortex of rat brain: (+)-*XXVIIb* is the active component of the racemate (see Table III).

A part of the compounds was tested within a general pharmacological screening program and only the positive results are mentioned here. Acute toxicity in mice, LD_{50} i.v. in mg/kg: *IIa*, 15; *IIb*, 30; *IIc*, 40; *IId*, 30; *IIe*, 25; *IIf*, 22·5; *IIId*, 30; *IIIe*, 25; *IVa*, 15; *IVb*, 35; *IVc*, 60; *IVd*, 30; *IVe*, 25; *IVf*, 50; *XXIe*, 50. Doses (D in mg/kg) used in the screening: *IIa*, 3; *IIb*, 6; *IIc*, 8; *IId*, 6; *IIe*, 5; *IIf*, 4; *IIId*, 6; *IIIe*, 5; *IVa*, 3; *IVb*, 7; *IVc*, 12; *IVd*, 6; *IVe*, 5; *IVf*, 10; *XXIe*, 10. Local anaesthetic effect (i) in the test of infiltration anaesthesia (concentration in % bringing about a complete anaesthesia in 50% of the guinea-pigs): *IIa*, 0·5; *IIb*, 0·5; *IIe*, 1; *IIIe*, 1; *IVa*, 0·5–1 (for procaine as the standard, ED = 1%); (ii) in the test of corneal anaesthesia (concentration in % bringing about in 50% rabbits the complete anaesthesia of the eye cornea): *IIa*, 1; *IIb*, 1; *IId*, 1; *IIe*, 1, *IIIe*, 1; *IVa*, 0·5; *IVb*, 1 (for trimecaine as the standard, ED = 1%). Hypotensive effect in normotensive anaesthetized rats: *IIa–IIf*, *IIIe*, *IVa–IVc*, *IVf*, and *XXIe* bring about brief and sharp drops of the blood pressure after doses D, administered intravenously. Spasmolytic effects on the isolated rat duodenum (concentrations in mg/l reducing the contractions to 50%) against spasms induced by (i) acetylcholine: *IIa* and *IIb*, 1–10; *IIIe*, 1–10; *XXIe*, 1–10; (ii) barium chloride: *IIa–IId*, 1–10; *IIf*, 10; *IIIe*, 1–10.

The compounds were also tested for antimicrobial activity in vitro (microorganisms and the minimum inhibitory concentrations in mg/l, unless they exceed 100 mg/l, are given): *Streptococcurs β-haemolyticus*, *XXIe* 50, *XXIIe* 50, *XXIIIf* 100, *XXIVb* 16, *XXIVc* 32, *XXVb* 8, *XXVIa* 16, *XXVIc* 8; *Streptococcus faecalis*, *XXIVb* 32, *XXIVc* 64, *XXVb* 8, *XXVc* 64, *XXVIa* 32, *XXVIb* 64, *XXVIc* 8; *Staphylococcus pyogenes aureus*, *XXIe* 25, *XXIf* 25, *XXIIe* 12·5, *XXIIf* 100, *XXIIIe* 100, *XXIIIf* 100, *XXIVb* 32, *XXIVc* 32, *XXVb* 16, *XXVIa* 64, *XXIX*·64; *Pseudomonas aeruginosa*, *XXI* 50, *XXIf* 100, *XXIIe* 50, *XXIIf* 100, *XXIIIe* 50, *XXIIIf* 50, *XXIVb* 64, *XXIVc* 64, *XXVb* 64, *XXVIc* 64; *Escherichia coli*, *XXIVb* 64; *Proteus vulgaris*, *IIe* 100, *IIId* 100, *IIIf* 100, *IVe* 100, *XXIe* 100, *XXIf* 50, *XXIIe* 50; *XXIIf* 25, *XXIII* 50, *XXIIIf* 25, *XXIVb* 64, *XXIVc* 64; *Trichophyton mentagrophytes*, *IIIf* 50, *XXIIe* 25, *XXIIf* 50, *XXIIIe* 50, *XXIIIf* 50, *XXIVc*, 50, *XXVc* 50, *XXVIb* 50.

EXPERIMENTAL

The melting points were determined in the Mettler FP-5 melting point recorder or in a Kofler block; the samples were dried in vacuo of about 60 Pa over P_2O_5 at room temperature or at a suitably elevated temperature. UV spectra (in methanol, λ_{max} in nm ($\log \varepsilon$)) were recorded with a Unicam SP 8 000 spectrophotometer, IR spectra (mostly in Nujol, ν in cm^{-1}) with a Perkin–Elmer 298 (mostly) or a Shimadzu IR-4 351 spectrophotometer, NMR spectra (in $CDCl_3$ unless stated otherwise, δ in ppm, J in Hz) mostly with the CW-NMR spectrometer Tesla BS 487C (^1H at 80 MHz) and partly with the FT-NMR spectrometer Tesla BS 567A (^1H at 100 MHz, ^{13}C at 25·14 MHz), and the mass spectra (m/z, fragments and/or %) with MCH 1 320 and/or Varian MAT 44S (GC-MS) spectrometers. The homogeneity of the products and composition of the mixtures were checked by thin-layer chromatography (TLC) on silica gel (Silufol). The extracts were dried with $MgSO_4$, Na_2SO_4 or K_2CO_3 and evaporated under reduced pressure on a rotary evaporator.

2-(3-Methoxyphenylthio)benzoic Acid (*XIb*)

A mixture of 8·24 g thiosalicylic acid, 100 ml dimethylformamide, 14·8 g K_2CO_3, 10·0 g 3-bromoanisole, and 1 g Cu was stirred and refluxed for 12 h. The mixture was diluted with 500 ml water, the solution was filtered and the filtrate was acidified with hydrochloric acid. The precipitated product was filtered, washed with water and crystallized from 100 ml 70% aqueous ethanol; 10·8 g (78%) of *XIb*, m.p. 169—170·5°C. Ref.[12], m.p. 173—174°C (different method).

2-(2,4-Dimethoxyphenylthio)benzoic Acid (*XId*) (Method *A*)

2,4-Dimethoxythiophenol[5,6] (50 g) was added to a stirred solution of 67 g KOH in 570 ml water, the mixture was heated to 55°C, treated with 72 g 2-iodobenzoic acid and 1·5 g Cu, and was refluxed for 14 h. The hot solution was filtered with active carbon, the filtrate was cooled and acidified with dilute hydrochloric acid. After standing overnight the precipitated product was filtered, washed with water, suspended in 1 l boiling ethanol, after cooling filtered again, and dried in vacuo; 70·8 g (84%) of *XId*, m.p. 211—214°C. Analytical sample, m.p. 215—217°C (ethanol). Analysis and spectra are included in Tables I and II.

2-(3-Methoxyphenylthio)benzaldehyde (*XIIb*)

A mixture of 20·0 g 3-methoxythiophenol[3], 40 ml dimethylformamide, 20 g K_2CO_3, and 20·1 g 2-chlorobenzaldehyde was stirred and heated for 5 h to 90°C. It was poured to 200 ml water and the product was extracted with benzene. Processing of the extract and crystallization of the crude product from 25 ml methanol gave 28·5 g (82%) of *XIIb*, m.p. 63·5—64·5°C. IR spectrum (Shimadzu IR-4351) (KBr): 689, 755, 842 (4 and 3 adjacent and solitary Ar–H); 1 231, 1 248, 1 282 ($ArOCH_3$); 1 574, 1 588 (Ar); 1 692, 2 729 (HC=O); 2 826 (OCH_3). ^1H NMR spectrum: 3·75 s, 3 H (OCH_3); 6·88 m, 3 H (H-2′, H-4′, H-6′); 7·25 m, 4 H (H-3, H-4, H-5, H-5′); 7·80 m, 1 H (H-6); 10·32 s, 1 H (CHO). ^{13}C NMR spectrum: 56·67 (OCH_3); 113·53 (C-2′); 117·34 (C-4′); 124·29 (C-6′); 125·93, 129·82, 130·64, 131·04 (C-3, C-4, C-5, C-6); 130·19 (C-5′); 133·48, 134·00 (C-2 and C-1′); 140·42 (C-1); 159·77 (C-3′); 190·84 (CHO). For $C_{14}H_{12}O_2S$ (244·3) calculated: 68·83% C, 4·95% H, 13·12% S; found: 68·59% C, 4·97% H, 12·95% S.

2-(2,4-Dimethoxyphenylthio)benzaldehyde (*XIId*)

Similar reaction of 30·0 g 2,4-dimethoxythiophenol[5,6], 24·3 g 2-chlorobenzaldehyde, and 18·7 g Na_2CO_3 in 55 ml dimethylformamide (3·5 h at 100°C under nitrogen) gave 42 g (89%) of crude

XIId, m.p. 115°C. Analytical sample, m.p. 129—130°C (ethanol). UV spectrum: 233 (4·43), infl. 265 (4·01), infl. 285 (3·79), 340 (3·54). IR spectrum: 760, 824, 842, 864 (4 and 2 adjacent and solitary Ar–H); 1 022, 1 076, 1 280, 1 300 ($ArOCH_3$); 1 480, 1 570, 1 585, 1 600, 3 010, 3 075 (Ar); 1 673, 1 690, 2 750, 2 810 (HC=O). ^{1}H NMR spectrum: 3·72 s and 3·80 s, 3 + 3 H (2 OCH_3); 6·40—7·50 m, 6 H (H-3, H-4, H-5, H-3′, H-5′, H-6′); 7·80 m, 1 H (H-6); 10·38 s, 1 H (CHO). For $C_{15}H_{14}O_3S$ (274·3) calculated: 65·67% C, 5·14% H, 11·69% S; found: 65·71% C, 5·16% H, 11·75% S.

2-(2,5-Dimethoxyphenylthio)benzaldehyde (*XIIe*)

Similar reaction of 32·8 g 2,5-dimethoxythiophenol[7], 26·6 g 2-chlorobenzaldehyde, and 20·5 g Na_2CO_3 in 60 ml dimethylformamide (3·5 h at 100°C under nitrogen) gave 43·5 g (84%) of *XIIe*, m.p. 92—95°C. Analytical sample, m.p. 97—98°C (ethanol). UV spectrum: infl. 268 (3·81), 305 (3·76), infl. 343 (3·53). IR spectrum: 762, 795, 850, 891 (4 and 2 adjacent and solitary Ar–H); 1 010, 1 040, 1 242, 1 296 ($ArOCH_3$); 1 490, 1 556, 1 580, 3 000, 3 060 (Ar); 1 675, 2 755 (HC=O). ^{1}H NMR spectrum: 3·65 s and 3·71 s, 3 + 3 H (2 OCH_3); 6·70—7·40 m, 6 H (H-3, H-4, H-5, H-3′, H-4′, H-6′); 7·80 m, 1 H (H-6); 10·35 s, 1 H (CHO). For $C_{15}H_{14}O_3S$ (274·3) calculated: 65·67% C, 5·14% H, 11·69% S; found: 65·77% C, 5·23% H, 11·79% S.

Semicarbazone, m.p. 205—207°C (aqueous ethanol). For $C_{16}H_{17}N_3O_3S$ (331·4) calculated: 57·99% C, 5·17% H, 12·68% N, 9·68% S; found: 57·58% C, 5·19% H, 12·54% N, 9·49% S.

2-(3-Methoxyphenylthio)benzoyl Chloride (*XIIIb*) (Method *B*)

A mixture of 30 g *XIb*, 250 ml benzene and 2 drops of dimethylformamide was stirred and treated with 45·1 g $SOCl_2$, added dropwise. The mixture was refluxed for 2 h, volatile components were evaporated in vacuo, the residue was dissolved in 55 ml boiling cyclohexane, the warm solution was filtered, and the filtrate was allowed to crystallize. After 2 h standing in a refrigerator, the product was filtered, washed with cyclohexane, and dried in vacuo; 30·4 g (95%) of *XIIIb*, m.p. 95—100°C. Analytical sample, m.p. 101—101·5°C (cyclohexane). UV spectrum: 224 (4·41), 253 (3·99), 280 (3·79), 320 (3·74). IR spectrum: 692, 725, 780, 790, 850, 860, 879 (4 and 3 adjacent and solitary Ar–H); 1 031, 1 130, 1 187, 1 250 ($ArOCH_3$); 1 480, 1 550, 1 588, 3 000, 3 080 (Ar); infl. 1 725, 1 757 (ArCOCl). ^{1}H NMR spectrum: 3·79 s, 3 H (OCH_3); 6·70—7·50 m, 7 H (ArH with the exception of H-6); 8·21 m, 1 H (H-6). For $C_{14}H_{11}ClO_2S$ (278·7) calculated: 60·32% C, 3·98% H, 12·72% Cl, 11·50% S; found: 60·38% C, 3·94% H, 13·06% Cl, 11·38% S.

N,N-Dimethyl-2-(3-methoxyphenylthio)benzamide (*XVIb*)

(i) (Method *C-1*). Chloride *XIIIb* (24·1 g) in 180 ml benzene was added dropwise at 10°C to 160 ml of stirred 20% aqueous dimethylamine. The mixture was stirred at room temperature for 2 h, the layers were separated, the benzene layer was washed with water, filtered, and evaporated in vacuo. The oily residue (23·1 g, 93%) crystallized on standing, m.p. 42—43°C. The analysis and spectra are included in Tables I and II.

(ii) A solution of 37·9 g *XIIIb* in 300 ml benzene was stirred and saturated at 25°C with 24·5 g dimethylamine and was allowed to stand for 48 h at room temperature. It was washed with 250 ml water, 200 ml 1M-HCl, 200 ml 5% NaOH, and 200 ml water. Processing gave 38·3 g (98%) of oily *XVIb*, which crystallized on standing, m.p. 42—43°C (product identical with that obtained under (i)).

(iii) A solution of 226 g dimethylamine hydrochloride in 150 ml water was slowly treated at 4—7°C with a solution of 89 g NaOH in 200 ml water (over 45 min under stirring). At the same

temperature, a solution of 83·2 g *XIIIb* in 640 ml toluene was added over 45 min under vigorous stirring. It was stirred for 2 h at room temperature, allowed to stand overnight, the toluene layer was separated, washed with water, and evaporated under reduced pressure. The oily residue (84·2 g, 97%) crystallized on standing, m.p. 42–43°C (product identical with that obtained under (i)).

3-Methoxythioxanthone (*XXXII*)

A solution of 10·0 g of supposed *XIIIb* (was stored for some time at room temperature) in 100 ml benzene was tried to react with a solution of 5·5 g diethylamine in 80 ml benzene at room temperature. After standing overnight the mixture was washed with dilute NaOH and water, dried, and evaporated. The semisolid residue crystallized after trituration with 30 ml light petroleum: 8·2 g of *XXXII*, m.p. 129–131°C (ethanol–heptane). Mass spectrum (CI and EI): 242 (M^+, $C_{14}H_{10}O_2S$, 100), 213 (8), 199 (22), 184 (8), 171 (35). UV spectrum: infl. 232 (4·17), infl. 250 (4·47), infl. 259 (4·53), 264 (4·54), infl. 280 (4·28), 308 (3·83), 365 (3·75). IR spectrum: 739, 823, 870 (4 and 2 adjacent and solitary Ar–H); 1 070, 1 272 ($ArOCH_3$); 1 483, 1 545, 1 597, 3 000, 3 050 (Ar); 1 631 (ArCOAr'). ^{1}H NMR spectrum: 3·92 s, 3 H (OCH_3); 7·02 m, 2 H (H-2, H-4); 7·55 m, 3 H (H-5, H-6, H-7); 8·60 m, 2 H (H-1, H-8). For $C_{14}H_{10}O_2S$ (242·3) calculated: 69·40% C, 4·16% H, 13·23% S; found: 69·51% C, 4·32% H, 13·40% S.

N,N-Di(2-propyl)-2-(3-methoxyphenylthio)benzamide (*XXIXb*) (Method *C-2*)

A stirred solution of 12·4 g di(2-propyl)amine in 100 ml benzene was treated at 5°C with a solution of 17·0 g *XIIIb* in 100 ml benzene and the mixture was stirred for 1 h at room temperature. After standing overnight the precipitated di(2-propyl)amine hydrochloride was filtered off, the filtrate was washed with 5% NaOH, 5% hydrochloric acid, and water, the solution was dried and evaporated. The residue crystallized from a mixture of 10 ml boiling benzene and 50 ml hexane; 16·0 g (76%) of *XIXb*, m.p. 98–100°C (benzene–hexane). Analysis and spectra are included in Tables I and II.

N,N-Dimethyl-2-(3-methoxyphenylthio)benzylamine (*IIb*)

(i) (Method *D-1*). A solution of 22·1 g *XVIb* in 350 ml ether was added over 40 min to a stirred solution of 8·7 g $LiAlH_4$ in 150 ml ether. The mixture was refluxed for 6 h and after cooling decomposed by slow addition of 9 ml water, 9 ml 15% NaOH, and 27 ml water. After stirring for 20 min the separated solid was filtered off and washed with ether. The filtrate was dried and evaporated. The residue, representing the almost homogeneous base *IIb* (19·5 g, 93%) resisted to all attempts at its crystallization. It was transformed to the hydrochloride (m.p. 149–150°C). The analyses and spectra are included in Tables I and II.

(ii) A solution of 57·5 g *XVIb* in 550 ml tetrahydrofuran, which was stirred under nitrogen, was treated with 22·0 g $NaBH_4$ and then at 20–27°C with 69 ml $BF_3.O(C_2H_5)_2$, added dropwise. The mixture was stirred for 1 h at room temperature and then refluxed for 3 h (permanently under nitrogen). After cooling it was dilued with 500 ml benzene, decomposed with 250 ml dilute hydrochloric acid (1 : 1) and made alkaline with 500 ml 20% NaOH (pH 8). The separated aqueous layer was extracted with benzene, the organic layers were combined, and evaporated. The residue (58·2 g) was extracted with 80 ml boiling ethanol and the undissolved solid (20·8 g) was filtered while hot. A sample (1·0 g) was crystallized from ethanol and identified to be N,N-dimethyl-2-(3-methoxyphenylthio)benzylamine borane (*XXXIII*), m.p. 71–75°C (ethanol).

IR spectrum: 770, 780, 809, 839 (Ar–H); 1 031, 1 250 ($ArOCH_3$); 1 170, 2 270, 2 360 (R_3N–BH_3); 1 481, 1 571, 1 590, 3 000, 3 035 (Ar). ^{1}H NMR spectrum (100 MHz): 2·60 s, 6 H ($N(CH_3)_2$); 3·73 s, 3 H (OCH_3); 4·30 s, 2 H ($ArCH_2N$); 6·60–7·60 m, 8 H (ArH). For $C_{17}H_{22}BNOS$ (287·2) calculated: 66·91% C, 7·72% H, 4·88% N; found: 66·98% C, 7·90% H, 5·03% N.

The solid amine borane was combined with the mother liquor, the mixture was diluted with 400 ml ethanol, 100 ml 20% NaOH were added and the mixture was refluxed for 8 h. Ethanol was evaporated in vacuo, the residue was distributed between 500 ml water and 200 ml benzene, the benzene layer was dried, and evaporated. The residue was dissolved in 50 ml ethanol and treatment with a solution of HCl in ether gave 54·0 g (87%) of hydrochloride of *IIb*, m.p. 148–151°C (ethanol–ether).

(iii) A solution of 68·7 g *XVIb* in 470 ml tetrahydrofuran was stirred under nitrogen and treated with 13·1 g $NaBH_4$ which was followed at 20–27°C by 68·7 g (61 ml) $BF_3.O(C_2H_5)_2$, added dropwise over 1 h. The mixture was stirred for 1 h at room temperature and refluxed for 3 h. After cooling the stirred mixture was treated with 190 ml dilute hydrochloric acid (1 : 1), added dropwise over 30 min. The mixture was refluxed for 3 h, cooled, and made alkaline with 400 ml 20% NaOH. The aqueous layer was diluted with 200 ml water, extracted with 1,2-dichloroethane, the organic layers were combined, dried, and evaporated. The residue was dissolved in 40 ml ethanol, the solution was treated with a slight excess of ethanolic HCl and 40 ml cyclohexane. The solution was seeded with some crystals of *IIb*-HCl and allowed to crystallize overnight in the refrigerator; 58·9 g (80%) of *IIb* hydrochloride, m.p. 147·5–150°C.

(iv) A mixture of 5·75 g *XVIb* and 20 ml $POCl_3$ was stirred for 3 h at room temperature and was evaporated in vacuo to dryness. The residue was diluted with 20 ml toluene which was also evaporated in vacuo for removing the residue of $POCl_3$. The residue (8·6 g) was dissolved in 15 ml tetrahydrofuran, the solution was cooled to 0°C and was treated over 1 h with a suspension of 1·5 g $NaBH_4$ in 40 ml ethanol. The mixture was stirred for 1 h at room temperature, was treated with 5 ml dilute hydrochloric acid (1 : 1), and refluxed for 6 h. Ethanol was evaporated in vacuo and the residue was distributed between benzene and dilute NH_4OH. The benzene solution was dried, benzene was evaporated, the residue was dissolved in 7 ml ethanol, and the solution was treated with ethanolic HCl; 1·1 g (18%) of *IIb* hydrochloride, m.p. 148–150·5°C (ethanol–ether).

The mother liquor was evaporated in vacuo, the residue was made alkaline with NH_4OH and was extracted with benezene. Processing of the extract gave 4·07 g of semi-solid substance which was treated with 40 ml ethanol and 8 ml 20% NaOH and the mixture was refluxed for 7 h. Ethanol was evaporated, the residue was distributed between water and benzene, and the benzene extract was processed. The residue (3·9 g) was crystallized from 4 ml ethanol and the crystalline substance (1·3 g) was recrystallized from a mixture of benzene and light petroleum; 0·15 g of 3-methoxythioxanthone (*XXXII*), m.p. 127–129·5°C, identical with the product described above. The mother liquors after the last crystallization were evaporated and the residue was crystallized twice from ethanol giving 0·50 g of a substance melting at 97–98°C which appears to be 3-methoxythioxanthene (*XXXV*). Mass spectrum: 228 (M^+, $C_{14}H_{12}OS$, 75), 227 (100), 213 (9), 212 (8), 197 (24), 184 (29), 152 (12), 139 (7), 114 (8). IR spectrum: 750, 813, 846, 890 (4 and 2 adjacent and solitary Ar–H); 1 030, 1 050, 1 242 ($ArOCH_3$); 1 490, 1 560, 1 583, 1 599, 3 000, 3 043, 3 065 (Ar). ^{1}H NMR spectrum (100 MHz): 3·80 s, 5 H (OCH_3 and $ArCH_2Ar'$); 6·77 dd, 1 H (H-2, J = 7·0; 2·5); 7·00 d, 1 H (H-4, J = 2·5); 7·18 d, 1 H (H-1, J = 7·0); 7·10–7·50 m, 4 H (remaining ArH). ^{13}C NMR spectrum: 38·17 t (C-9); 55·42 q (OCH_3); 111·97 d (C-2); 112·79 d (C-4); 126·46 d, 126·61 d, 126·83 d (C-5, C-6, C-7); 127·95 d (C-8); 128·25 s (C-9a); 128·55 d (C-1); 133·71 s (C-10a); 134·83 s (C-4a); 136·62 s (C-8a), 158·28 s (C-3). For $C_{14}H_{12}OS$ (228·3) calculated: 73·65% C, 5·30% H, 14·04% S; found: 73·66% C, 5·40% H, 13·96% S.

(v) A mixture of 28·5 g *XIIb*, 43 g dimethylformamide and 26·8 g formic acid was stirred and refluxed for 6·5 h (bath temperature 180°C). After cooling the mixture was treated with 170 ml 5% hydrochloric acid and the solution was washed with ether (these washings were the source of neutral by-products). The acid aqueous solution was made alkaline with 20% NaOH an the base was extracted with 1,2-dichloroethane. Processing of the extract gave 30·3 g of crude *IIb* which was transformed to hydrochloride (27·1 g, 75%), m.p. 149—150°C.

The ethereal washings from several batches were combined and evaporated. The residue (20 g) was chromatographed on 200 g silica gel. A mixture of benzene and light petroleum eluted first 4·6 g of a substance melting at 91—96°C, corresponding by the TLC comparison to *XXXV* from the preceding experiment. Elution with benzene gave a homogeneous oily fraction (1·5 g) which was identified by spectra as 2-(3-methoxyphenylthio)benzyl formate (*XXXVI*). Mass spectrum: 274 (M^+, $C_{15}H_{14}O_3S$), 227 ($C_{14}H_{11}OS$), 213 ($C_{13}H_9OS$), 197 ($C_9H_9O_3S$). ^{1}H NMR spectrum (100 MHz): 3·72 s, 3 H (OCH_3); 5·34 s, 2 H ($ArCH_2O$); 6·75—7·50 m, 8 H (ArH); 8·10 s, 1 H (CHO). ^{13}C NMR spectrum: 55·95 (OCH_3); 64·61 (CH_2); 112·49 (C-2′); 115·11 (C-4′); 122·05 (C-6′); 129·07, 129·98, 130·21, 134·08 (C-3, C-4, C-5, C-6); 130·72 (C-5′); 134·08 (C-1′); 136·84 (C-2); 137·07 (C-1); 160·50 (C-3′); 161·27 (CHO, J_{C-H} = 225 Hz). The last benzene fraction (0·36 g) was identified again as *XXXII*, m.p. 129·5—130·5°C (ethanol), identical with the compound described in the foregoing paragraphs.

N,N-Dimethyl-2-(2,4-dimethoxyphenylthio)benzylamine (*IId*)

(i) The compound was prepared from *XVId* by method *D-1* in the yield of 80%; the oily base was transformed to hydrogen maleate (m.p. 117—118°C) and hydrobromide (m.p. 208—209°C). Analyses of the salts and spectra of the base are included in Tables I and II.

(ii) A stirred suspension of 27·6 g *XIId* in 400 ml ethanol was treated dropwise with a solution of 1·9 g $NaBH_4$ in 18 ml water containing 0·2 ml 20% NaOH and the mixture was refluxed 6 h. Ethanol was evaporated and the residue was distributed between water and benzene. The benzene layer was washed with 2% NaOH and water, dried, filtered with active carbon, and evaporated; 27·2 g (98%) of 2-(2,4-dimethoxyphenylthio)benzyl alcohol (m.p. 87—88°C) which was used without further characterization.

A boiling solution of 27·0 g of the preceding product in 60 ml benzene was treated under stirring over 30 min with 17·5 g $SOCl_2$, the mixture was further refluxed for 15 min, and the volatile components were completely removed by evaporation. The crystalline residue was recrystallized from a mixture of 35 ml benzene and 15 ml light petroleum; 18·0 g (63%) of 2-(2,4-dimethoxyphenylthio)benzyl chloride (m.p. 91—93°C) which also was processed without further characterization.

The preceding chloro compound (18·0 g) was dissolved in 80 ml chloroform and the solution was saturated at 20°C with 11 g gaseous dimethylamine. The mixture was transferred to a 250 ml autoclave and it was heated for 12 h to 75°C. After cooling chloroform was evaporated, the residue was distributed between water and benzene and the benzene layer was washed with 10% NaOH and with water. The base was transferred by shaking to 300 ml 1·5M-HCl, the acid aqueous layer (with crystallizing hydrochloride) was made alkaline with NH_4OH and the base was extracted with benzene. Processing gave 17·5 g (95%) of the oily *IId* (hydrogen maleate, m.p. 117—118°C), a sample of which was transformed to the picrate, m.p. 180—181°C (acetone). For $C_{23}H_{24}N_4O_9S$ (532·5) calculated: 51·87% C, 4·54% H, 10·52% N, 6·02% S; found: 51·87% C, 4·62% H, 10·42% N, 6·20% S.

N,N-Dimethyl-2-(3,4-dimethoxyphenylthio)benzylamine (*IIf*) (Method *D-2*)

A solution of 23·2 g *XVIf* in 200 ml tetrahydrofuran was added dropwise over 40 min to a stirred solution of 7·2 g $LiAlH_4$ in 150 ml tetrahydrofuran and the mixture was refluxed for 8 h. After cooling and under external cooling it was decomposed by slow addition of 7 ml water, 7 ml 15% NaOH, and 21 ml water. After 20 min of stirring the solid was filtered off, washed with tetrahydrofuran, and the filtrate was evaporated; 19·1 g (86%) of oily *IIf*. Hydrochloride, m.p. 175—176°C (ethanol–ether). Analysis of the hydrochloride is included in Table I.

N,N-Diethyl-2-(2-methoxyphenylthio)benzylamine (*Va*) (Method *D-3*)

A solution of 14·4 g *XVIIa* in a mixture of 50 ml benzene and 100 ml ether was added dropwise to a stirred solution of 6·0 g $LiAlH_4$ in 50 ml ether and the mixture waz refluxed for 6 h. After standing overnight it was decomposed by addition of 30 ml 20% NaOH, the mixture was refluxed for 1 h, cooled and filtered. The filtrate was evaporated in vacuo, the residue was dissolved in 100 ml benzene and the base was transferred by shaking into 100 ml dilute hydrochloric acid (1 : 3). From the aqueous layer it was released with dilute NaOH and isolated by extraction with benzene; 10·2 g (74%) of oily *Va*. Hydrochloride, m.p. 182—184°C (ethanol–ether). Analysis and spectra of the hydrochloride are included)n Tables I and II.

2-(3-Hydroxyphenylthio)benzoic Acid (*XXXb*)

3-Hydroxythiophenol[26] (75%, the purity estimated on the basis of content of sulfur) (20·3 g), 39·7 g 2-iodobenzoic acid, and 3·0 g Cu were added to a stirred solution of 25 g KOH in 250 ml water and the mixture was refluxed for 6·5 h. After cooling it was filtered and the filtrate was acidified with hydrochloric acid. After standing overnight, the crude product was filtered. Two crystallizations from aqueous ethanol gave 22·15 g of homogeneous *XXXb*, m.p. 209—211°C. UV spectrum: 252 (3·90), 282 (3·72), 315 (3·63). IR spectrum: 694, 735, 782, 870 (4 and 3 adjacent and solitary Ar–H); 1 209 (ArOH); 1 480, 1 559, 1 585, 3 050 (Ar); 1 671, 2 670 (ArCOOH); 3 230, 3 325 (OH). ^{1}H NMR spectrum (CD_3SOCD_3, 100 MHz): 6·95 m, 4 H (H-3, H-2′, H-4′, H-6′); 7·35 m, 3 H (H-4, H-5, H-5′); 7·95 bd, 1 H (H-6, J = 8·5). For $C_{13}H_{10}O_3S$ (246·3) calculated: 63·40% C, 4·09% H, 13·02% S; found: 62·89% C, 4·33% H, 12·81% S.

N,N-Dimethyl-2-(3-hydroxyphenylthio)benzamide (*XXXIb*)

A mixture of 13·1 g triphenylphosphine, 20 ml tetrachloromethane and 100 ml tetrahydrofuran was stirred for 1 h, 12·1 g *XXXb* and 7·0 g dimethylamine were added, the mixture was stirred for 4 h, allowed to stand overnight, stirred for 3 h, filtered and the filtrate was evaporated. The inhomogeneous residue was chromatographed on 150 g silica gel using elution with chloroform. The first fractions contained the less polar components (triphenylphosphine, m.p. 78 to 79·5°C, and triphenylphosphine oxide, m.p. 155—159°C). The last fractions crystallized from ether; 3·62 g (27%) of homogeneous *XXXIb*, m.p. 124·5—125·5°C. UV spectrum: 248 (4·14), 280 (3·77). IR spectrum: 690, 699, 745, 770, 864, 890 (4 and 3 adjacent and solitary Ar–H); 1 258 (ArOH); 1 587, 3 050 (Ar); 1 615 ($ArCONR_2$); 2 575, 2 660, 2 700, 2 780 (NH^+); infl. 3 200 (OH). ^{1}H NMR spectrum (100 MHz): 2·85 s and 3·11 s, 3 + 3 H ($N(CH_3)_2$); 6·70—7·30 m, 8 H (ArH); 8·36 bs, 1 H (OH). For $C_{35}H_{15}NO_2S$ (273·4) calculated: 65·91% C, 5·53% H, 5·12% N, 11·73% S; found: 66·21% C, 5·60% H, 4·88% N, 11·76% S.

N,N-Dimethyl-2-(3-hydroxyphenylthio)benzylamine (*XXIb*)

(i) (Method *E*). A mixture of 7·0 g *IIb* and 14·8 g pyridine hydrochloride was stirred and heated for 30 min to 210—220°C (bath temperature). After partial cooling the melt was dissolved in 220 ml water and the solution was filtered with active carbon. The filtrate was made alkaline to pH 8—8·5 and the separated oil was extracted with chloroform. Processing of the extract gave 5·6 g (84%) of oily *XXIb* which was converted to salts: hydrogen maleate, m.p. 123—124°C (ethanol–ether); hydrochloride, m.p. 165—166°C (ethanol); hydrobromide, m.p. 150—151°C (ethanol–ether). The pure hydrogen maleate was decomposed with NH_4OH, the oily base was isolated by decantation and was induced to crystallize by trituration with light petroleum, m.p. 106—107°C (cyclohexane). Analyses and spectra of the base and the salts are included in Tables I and II.

(ii) (Method *F*). A solution of 7·7 g *IIb* in 60 ml chloroform was cooled to 10°C and was treated under stirring over 15 min with a solution of 14·0 g BBr_3 in 20 ml chloroform. The mixture was stirred for 6 h at room temperature, allowed to stand overnight, and diluted at 10—15°C with 65 ml ethanol, added dropwise. The clear solution formed was stirred for 8 h at room temperature and the solvents were evaporated at 50—60°C under reduced pressure. The oily residue crystallized on trituration with ether; 7·7 g (75%) of *XXIb* hydrobromide, m.p. 142—145°C. Single crystallization from ethanol gave the pure substance melting at 150°C identical with that obtained under (i).

(iii) A mixture of 214 g *IIb*.HCl and 850 ml 47% hydrobromic acid was stirred and heated for 8 h to 120°C. After cooling it was poured into 1·85 l water and it was made slightly alkaline by slow addition of 1·2 l 20% NaOH (pH 9). It was extracted with 2·5 l 1,2-dichloroethane and processing of the extract gave 170 g (95%) of crystalline *XXIb*, m.p. 107—108°C (methanol), identical with the base described under (i).

(iv) A solution of 1·4 g *XXXIb* in 20 ml tetrahydrofuran was added over 10 min to a solution of 1·0 g $LiAlH_4$ in 20 ml tetrahydrofuran and the mixture was refluxed for 6 h. After cooling it was decomposed under stirring with 5 ml water, added dropwise. The solid was filtered off, washed with tetrahydrofuran, the filtrate was dried and evaporated; 1·0 g (76%) of oily *XXIb*. It was converted to hydrogen maleate, m.p. 123—127°C, corresponding to the product described under (i).

1-(2-(3-Methoxyphenylthio)phenyl)ethanol (*XXXVII*)

Grignard reagent was prepared from 60 g methyl iodide and 10·2 g Mg in 250 ml ether and was treated under stirring with a solution of 67·8 g *XIIb* in 250 ml of the mixture of ether and benzene (1 : 1), added dropwise over 30 min. It was refluxed for 3 h, after cooling it was decomposed with 200 ml 20% NH_4Cl, the separated organic layer was dried and evaporated; 73 g (theoretical) of crude *XXXVII*. A sample for analysis was distilled, b.p. 183°C/1 kPa. ^{1}H NMR spectrum (100 MHz): 1·44 d, 3 H (C–CH_3, J = 6·0); 2·2 d, 1 H (OH, J = 4·0); 3·72 s, 3 H (OCH_3); 5·40 m, 1 H (Ar–CH–O); 6·75 m, 2 H (H-2′, H-4′); 7·00—7·50 m, 5 H (H-3, H-4, H-5, H-5′, H-6′); 7·65 m, 1 H (H-6). For $C_{15}H_{16}O_2S$ 260·4) calculated: 69·20% C, 6·29% H, 12·32% S, found: 69·49% C, 6·14% H, 12·45% S.

1-(2-(3-Methoxyphenylthio)phenyl)ethyl Chloride (*XXXVIII*)

A refluxing mixture of 71·2 g *XXXVII*, 250 ml benzene and 1 drop of dimethylformamide was treated over 30 min with 30 ml $SOCl_2$, added dropwise. The mixture was refluxed for 1·5 h and processed by distillation; 70 g (92%) of *XXXVIII*, b.p. 177—180°C/0·2 kPa. ^{1}H NMR spectrum

(100 MHz): 2·78 d, 3 H (C–CH_3, J = 7·0); 3·76 s, 3 H (OCH_3); 5·84 q, 1 H (Ar–CH–Cl, J = = 7·0); 6·75 m, 2 H (H-2′, H-4′); 7·10—7·60 m, 5 H (H-3, H-4, H-5, H-5′, H-6′); 7·78 m, 1 H (H-6). For $C_{15}H_{15}ClOS$ (278·8) calculated: 12·72% Cl, 11·50% S; found: 12·50% Cl, 11·53% S.

N,N-Dimethyl-1-(2-(3-methoxyphenylthio)phenyl)ethylamine (*VIIIb*)

A mixture of 28·7 g *XXXVIII*, 200 ml dioxane and 29 g liquid dimethylamine was heated in the autoclave for 6 h to 90°C. After cooling the mixture was evaporated in vacuo, the residue was diluted with water and extracted with benzene. From the benzene extract the base was transferred by shaking into dilute hydrochloric acid. Evaporation of the benzene layer recovered 10·9 g of the starting *XXXVIII*. The acid aqueous layer was made alkaline with 20% NaOH, and the base was isolated by extraction with benzene; 18·3 g (theoretical per conversion) of racemic oily *VIIIb*.

Hydrochloride, m.p. 123—126°C (ethanol). For $C_{17}H_{22}ClNOS$ (323·9) calculated: 63·04% C, 6·85% H, 10·95% Cl, 4·32% N, 9·90% S; found: 63·11% C, 6·69% H, 11·00% Cl, 4·15% N, 9·91% S.

N,N-Dimethyl-1-(2-(3-hydroxyphenylthio)phenyl)ethylamine (*XXVIIb*)

Racemic oily *VIIIb* (19·2 g) was stirred and heated for 7 h with 100 ml 48% hydrobromic acid to 120—130°C (bath temperature). It was diluted with 250 ml water and after standing overnight the crystallized hydrobromide of *XXVIIb* was filtered, washed with a small quantity of ice-cold water, and dried in vacuo; 22·7 g (95%), m.p. 194—196°C. Analytical sample, m.p. 195—196°C (ethanol–ether). For $C_{16}H_{20}BrNOS$ (354·3) calculated: 54·24% C, 5·69% H, 22·55% Br, 3·95% N, 9·05% S; found: 54·38% C, 5·60% H, 22·54% Br, 3·79% N, 8·85% S.

The base was released with NH_4OH, isolated by extraction with ether and crystallized from methanol, m.p. 107—108·5°C. UV spectrum: 204 (4·47), infl. 211 (4·45), 246 (3·98), 280 (3·72), infl. 292 (3·63). IR spectrum: 690, 759, 775, 895 (4 and 3 adjacent and solitary Ar–H); 1 263 (ArOH); 1 490, 1 582, 1 595, 2 995, 3 045 (Ar); 2 570, 2 660 (NH^+); 2 780 (N–CH_3). ^{1}H NMR spectrum (100 MHz): 1·25 d, 3 H (C–CH_3, J = 6·0); 2·15 s, 6 H ($N(CH_3)_2$); 4·06 q, 1 H (Ar–CH–N, J = 6·0); 6·50—7·60 m, 9 H (ArH and OH). For $C_{16}H_{19}NOS$ (273·4) calculated: 70·29% C, 7·01% H, 5·12% N, 11·73% S; found: 70·41% C, 7·07% H, 5·08% N, 12·11% S.

(−)-*XXVIIb*: Neutralization of 20 g racemic *VIIIb* with 27·6 g (−)-O,O′-dibenzoyl-L-tartaric acid in 100 ml ethyl acetate gave 39·5 g diastereoisomeric mixture of hydrogen (−)-O,O′-dibenzoyl-L-tartrates which was crystallized three times from a mixture of ethyl acetate and acetone to give 10·0 g of one homogeneous diastereoisomer, m.p. 123—126°C, $[\alpha]_D^{20}$ −38·84°, $[\alpha]_{365}^{20}$ −211·72° (c = 1, ethanol). For $C_{35}H_{35}NO_9S$ (645·7) calculated: 65·10% C, 5·46% H, 2·17% N, 4·97% S; found: 65·34% C, 5·41% H, 2·08% N, 5·01% S. This salt was decomposed with NH_4OH and the released base (3·5 g, isolated by extraction with ether) was heated with 25 ml 48% HBr for 8 h to 120°C. After cooling it was diluted with water and the little soluble hydrobromide of (−)-*XXVIIb* was filtered; 2·9 g, m.p. 213·5—214·5°C (ethanol), $[\alpha]_D^{20}$ +40·94°, $[\alpha]_{365}^{20}$ +194·42° (c 1, ethanol). For $C_{17}H_{20}BrNOS$ (354·3) calculated: 54·24% C, 5·69% H, 22·55% Br, 3·95% N, 9·05% S; found: 54·33% C, 5·84% H, 22·35% Br, 3·88% N, 9·08% S. The released (−)-base was crystallized from methanol, m.p. 97·5—99°C, $[\alpha]_D^{20}$ −42·6°, $[\alpha]_{365}^{20}$ −165·5° (c 1, ethanol). For $C_{16}H_{19}NOS$ (273·4) calculated: 70·29% C, 7·01% H, 5·12% N, 11·73% S; found: 70·29% C, 7·18% H, 5·00% N, 11·78% S.

(+)-*XXVIIb*: Mother liquors from the preceding resolution were combined and the released base (16 g) was neutralized with 22 g (+)-O,O′-dibenzoyl-D-tartaric acid in 200 ml of a mixture

of acetone and ethyl acetate (1 : 1) and the diastereoisomeric mixture obtained was crystallized three times from the same mixture of solvents; 13·8 g of the homogeneous diastereoisomer, m.p. 125·5–127·5°C, $[\alpha]_D^{20}$ +36·25°, $[\alpha]_{365}^{20}$ +200·3° (*c* 1, ethanol). This salt was decomposed with NH_4OH and the base (5·9 g) was extracted with ether. After evaporation of the solvent it was heated for 8 h with 50 ml 48% HBr to 120°C. After cooling it was diluted with water and 7·0 g of hydrobromide of (+)-*XXVIIb* crystallized, m.p. 213·5–214·5°C (ethanol), $[\alpha]_D^{20}$ −41·33°, $[\alpha]_{365}^{20}$ −192·25° (*c* 1, ethanol). For $C_{16}H_{20}BrNOS$ (354·3) calculated: 54·24% C, 5·64% H, 22·55% Br, 3·95% N; found: 54·08% C, 5·88% H, 22·33% Br, 3·73% N. The released (+)-*XXVIIb* crystallized from methanol and melted at 98·5–99·5°C, $[\alpha]_D^{20}$ +45·36°, $[\alpha]_{365}^{20}$ +174·97° (*c* 1, ethanol). For $C_{16}H_{19}NOS$ (273·4) calculated: 70·29% C, 7·01% H, 5·12% N, 11·73% S; found: 70·29% C, 7·17% H, 5·05% N, 11·82% S.

N-(2-Dimethylaminoethyl)-2-(3-methoxyphenylthio)benzylamine (*IXb*)

A solution of 12·0 g 2-dimethylaminoethylamine in 50 ml benzene was stirred and treated under external cooling (10–20°C) over 10 min with a solution of 15·0 g *XIIIb* in 150 ml benzene and the mixture was stirred for 4 h at room temperature. After standing overnight it was washed with water, dried, and benzene was evaporated; 17·8 g (theoretical) of the crude oily N-(2-dimethylaminoethyl)-2-(3-methoxyphenylthio)benzamide (*XXb*), which was further used without characterization.

The whole quantity of the crude *XXb* was dissolved in 100 ml tetrahydrofuran, the solution was treated with 4·3 g $NaBH_4$ and the stirred mixture was treated under nitrogen with 15 g $BF_3.O(C_2H_5)_2$, added dropwise. The mixture was stirred for 1 h at room temperature and was refluxed for 3 h. After cooling, 20 ml hydrochloric acid were added and the mixture was refluxed for 3 h. After cooling it was made alkaline with 100 ml 20% NaOH and the base was extracted with ether. Processing of the extract gave 16·5 g of crude oily *IXb* which was transformed to the dihydrochloride, m.p. 174–177°C (ethanol). ^{1}H NMR spectrum (CD_3SOCD_3, 100 MHz): 2·86 s, 6 H ($N(CH_3)_2$); 3·74 s, 3 H (OCH_3); 3·00–3·80 m, 4 H (NCH_2CH_2N); 4·37 bs, 2 H ($ArCH_2N$); 6·85 m, 3 H (H-2′, H-4′, H-6′); 7·30 t, 1 H (H-5′); 7·62 m, 3 H (H-3, H-4, H-5); 7·92 m, 1 H (H-6). For $C_{18}H_{26}Cl_2N_2OS$ (389·4) calculated: 55·52% C, 6·73% H, 18·21% Cl, 7·19% N, 8·23% S; found: 55·48% C, 6·88% H, 18·12% Cl, 6·90% N, 8·21% S.

N-Methyl-N-(2-dimethylaminoethyl)-2-(3-methoxyphenylthio)benzylamine (*Xb*)

A mixture of 15·0 g *IXb*, 12 ml formic acid, and 18 ml 36% aqueous formaldehyde was stirred and heated to 100°C for 3 h. After cooling it was acidified with 10 ml hydrochloric acid, washed with ether, the aqueous layer was made alkaline with NH_4OH and extracted with ether. Processing of the extract gave 9·0 g of crude oily *Xb* which was transformed to dihydrochloride, m.p. 168 to 175°C (ethanol–ether). Mass spectrum: 330 (M^+, $C_{19}H_{28}Cl_2N_2OS$), 272, 229, 214, 197. IR spectrum: 690, 755, 789, 865 (4 and 3 adjacent and solitary Ar–H); 1 031, 1 250 ($ArOCH_3$); 1 480, 1 590, 3 010, 3 045, 3 070 (Ar); 2 445, 2 500, 2 560 (NH^+). ^{1}H NMR spectrum (CD_3SOCD_3, 100 MHz): 2·70 s, 3 H ($N-CH_3$); 2·86 s, 6 H ($N(CH_3)_2$); 3·70 s, 3 H (OCH_3); 3·75 s, 4 H (NCH_2CH_2N); 4·60 bs, 2 H ($ArCH_2N$); 6·90–8·10 m, 8 H (ArH). For $C_{19}H_{28}Cl_2.N_2OS$ (403·4) calculated: 56·57% C, 7·00% H, 17·58% Cl, 6·94% N, 7·95% S; found: 56·20% C, 7·19% H, 17·49% Cl, 6·76% N, 8·14% S.

N-(2-Dimethylaminoethyl)-2-(3-hydroxyphenylthio)benzylamine (*XXVIIIb*)

A mixture of 2·55 g *IXb*-HCl and 20 ml 48% HBr was stirred for 6·5 h at 120°C. After cooling it was diluted with water, made alkaline with NH_4OH, and extracted with chloroform. Pro-

cessing of the extract gave 2·35 g of crude oily *XXVIIIb* which was transformed to bis(hydrogen maleate) (3·5 g, theoretical), m.p. 152·5–153·5°C (ethanol). ^{1}H NMR spectrum (CD_3SOCD_3, 100 MHz): 2·78 s, 6 H ($N(CH_3)_2$); 3·18 m, 4 H (NCH_2CH_2N); 4·17 s, 2 H ($ArCH_2N$); 6·14 s, 4 H (2 CH=CH of maleic acid); 6·60–7·60 m, 8 H (ArH). For $C_{25}H_{30}N_2O_9S$ (534·6) calculated: 56·17% C, 5·66% H, 5·24% N, 6·00% S; found: 55·69% C, 5·75% H, 5·13% N, 6·23% S.

N-Methyl-N-(2-dimethylaminoethyl)-2-(3-hydroxyphenylthio)benzylamine (*XXIXb*)

A mixture of 3·85 g *Xb*-2 HCl and 25 ml 48% HBr was heated for 7 h to 120°C, cooled, diluted with water, made alkaline with NH_4OH, and extracted with chloroform. Processing of the extract gave 3·4 g of crude oily *XXIXb* which was transformed to bis(hydrogen maleate) (5·15 g, 98%), m.p. 148–151·5°C (ethanol). Mass spectrum: 316 (M^+, $C_{18}H_{24}N_2OS$, 0·1), 258 (40), 215 (47), 213 (53), 98, 58 (100). UV spectrum: 246 (4·07), 280 (3·79). IR spectrum: 682, 753, 777, 869, 889 (4 and 3 adjacent and solitary Ar–H); 1 353, 1 589 (COO^-); 1 619 (C=C); 1 709 (COOH); 2 400 (NH^+); 3 160, 3 320 (OH). ^{1}H NMR spectrum (CD_3SOCD_3, 100 MHz): 2·18 s, 3 H ($N-CH_3$); 2·78 s, 6 H ($N(CH_3)_2$); 2·76 bm and 3·14 btm, 2 + 2 H (NCH_2CH_2N); 4·70 s, 2 H ($ArCH_2N$); 6·12 s, 4 H (2 CH=CH of maleic acid); 6·60–7·30 m, 8 H (ArH). For $C_{26}H_{32}N_2O_9S$ (548·6) calculated: 56·92% C, 5·88% H, 5·11% N, 5·84% S; found: 56·70% C, 6·11% H, 5·05% N, 5·89% S.

N,N-Dimethyl-2-(3-hydrophenylthio)benzylamine S-Oxide (*XXXIX*)

A solution of 3·75 g *XXIb* hydrogen maleate in 30 ml acetic acid was treated with 2 ml 30% H_2O_2. After 12 h standing at room temperature the mixture was diluted with water, made alkaline with NH_4OH, and extracted with ether; 1·87 g (68%) of *XXXIX*, m.p. 140·5–142°C (methanol). UV spectrum: 281 (3·38). IR spectrum: 690, 757, 790, 878 (4 and 3 adjacent and solitary Ar–H); 1 020 (Ar–SO–Ar'); 1 250 (ArOH); 1 486, 1 584, 1 602, 3 020, 3 060, 3 090 (Ar); 2 776, 2 820, 2 850 ($N-CH_3$); 3 160, 3 220 (OH). ^{1}H NMR spectrum (100 MHz): 2·08 s, 6 H ($N(CH_3)_2$); 3·16 d and 3·75 d (ABq), 1 + 1 H ($ArCH_2N$, J = 13·0); 6·70–7·60 m, 8 H (OH and ArH with the exception of H-3); 8·05 m, 1 H (H-3). For $C_{15}H_{17}NO_2S$ (275·4) calculated: 65·34% C, 6·22% H, 5·09% N, 11·64% S; found: 65·38% C, 6·22% H, 5·10% N, 11·80% S.

N,N-Dimethyl-2-(3-hydroxyphenylthio)benzylamine S,S-Dioxide (*XL*)

A solution of 3·75 g *XXIb* hydrogen maleate in 30 ml acetic acid was treated with 5 ml 30% H_2O_2 and the mixture was allowed to stand for 3 days at room temperature. It was diluted with water, made alkaline with NH_4OH and extracted with chloroform. The extract was evaporated, the residue was extracted with ether and the extract was evaporated; 0·74 g (25%) of *XL*, m.p. 128–129·5°C (ether). UV spectrum: infl. 269 (3·40), 276 (3·49), 288 (3·51). IR spectrum: 690, 716, 762, 791, 830, 869 (4 and 3 adjacent and solitary Ar–H), 1 150, 1 305 (SO_2); 1 273 (ArOH); 1 572, 1 590, 1 602, 3 000, 3 025, 3 060 (Ar); 2 490, 2 570, 2 685 (NH^+); 2 785 ($N-CH_3$). ^{1}H NMR spectrum: 2·09 s, 6 H ($N(CH_3)_2$); 3·77 s, 2 H ($ArCH_2N$); 7·00 m, 1 H (H-2'); 7·10 to 7·80 m, 7 H (H-4, H-5, H-6, H-4', H-5', H-6', OH); 8·12 m, 1 H (H-3). For $C_{15}H_{17}NO_3S$ (291·4) calculated: 61·83% C, 5·88% H, 4·81% N, 11·01% S; found: 61·66% C, 5·81% H, 4·61% N, 11·07% S.

N,N-Dimethyl-2-(3-hydroxyphenylthio)benzylamine N,S,S-Trioxide (*XLI*)

A solution of 3·75 g *XXI* hydrogen maleate in 30 ml acetic acid was treated with 8 ml 30% H_2O_2 and the mixture was allowed to stand for 7 days at room temperature. It was then diluted with

water, neutralized with NH_4OH to pH 8 and extracted with chloroform. Processing of the extract gave 2·0 g of glassy substance which crystallized after trituration with ether. It was recrystallized first form benzene–ethanol and then from ethanol–ether yielding 0·70 g (23%) of *XLI*, m.p. 164·5—166·5°C. UV spectrum: infl. 272·5 (3·41), 278 (3·49), 291 (3·49). IR spectrum: 715, 781, 798, 891 (Ar–H); 923 (N–O); 1 151, 1 295 (SO_2); 1 236 (ArOH); 1 553, 1 581, 3 010, 3 032, 3 092 (Ar); 2 630 (NH^+). ^{1}H NMR spectrum (CD_3SOCD_3, 100 MHz): 2·42 s, 6 H ($N(CH_3)_2$); 4·92 s, 2 H ($ArCH_2N$); 7·00—7·80 m, 7 H (ArH with the exception of H-6); 8·10 m, 1 H (H-6). For $C_{15}H_{17}NO_4S$ (307·4) calculated: 58·61% C, 5·57% H, 4·56% N, 10·43% S; found: 58·38% C, 5·54% H, 4·48% N, 10·47% S.

Repeated extraction of the aqueous solution with chloroform led to 0·44 g of a different substance which was identified as *XL*, m.p. 128—129·5°C.

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