CCA-489

547.755.07:546.22
Original Scientific Paper

Indole Compounds. V*. 3-(2-Mercaptoethyl)indoles and *bis*-[3-(2-Thioethyl)indoles], Sulphur Analogs of Tryptophol, 5-Hydroxytryptophol, and Other *Bz*-Substituted Tryptophols

D. Keglević, D. Desaty, D. Goleš, and L. Stančić

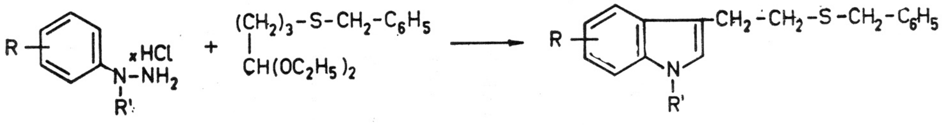
Tracer Laboratory, Institute »Ruđer Bošković«, Zagreb, Croatia, Yugoslavia

Received November 3, 1967

The one-step cyclization of 4-benzylthiobutanal diethyl acetal with various hydrazine hydrochlorides under mild conditions is described. The obtained 3-(2-benzylthioethyl)indoles were debenzylated with sodium in liquid ammonia to the corresponding 3-(2-mercaptoethyl)indoles and *bis*-[3-(2-thioethyl)indoles], the sulphur analogs of tryptophols.

In previous papers of this series[1–4] the indolization under mild conditions of phenylhydrazine hydrochlorides bearing an electron-releasing group in *para*-, or less favourably in *ortho*-position, with various aliphatic acetals was described. The resulting 5- and 7- substituted tryptamines, their *N*-acyl and *N*,*N*-disubstituted derivatives, respectively, were obtained in very good to fair yields. In addition, this modified Fischer indole synthesis proved to be a method of choice for the preparation[4] of 5-substituted indole-3-acetonitriles.

The reaction has now been extended to include the synthesis of some indole thioethers. Thioethers in which the sulphur atom is directly linked to the indole nucleus at position 2-[5], 3-[6,7], 4-[8], 5-[8–10], 6-[8] and 7-[8] respectively, have already been described in the literature; some of them were also converted to the corresponding mercaptans[8,9] and disulphides[7,11]. Our purpose in conducting the present study was to find out a synthetic route to 3-(2-mercaptoethyl)indoles, the hitherto undescribed thiol analogs of tryptophols. It seemed to us that the corresponding *S*-benzyl derivatives would be suitable intermediates in this pathway, and that some of them might be formed by the direct indolization. If so, 3-(2-benzylthioethyl)indoles with an electron-releasing group in position 5- or 7- should be available from the condensation of 4-benzylthiobutanal diethyl acetal (I) with the corresponding phenylhydrazine hydrochlorides.



II – VII

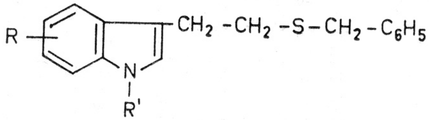
The acetal I was obtained smoothly by addition of benzylmercaptan to vinylethanal diethyl acetal. The condensation with phenylhydrazines was per-

---

* Part IV.: D. Desaty and D. Keglević, *Croat. Chem. Acta* **37** (1965) 25.

TABLE I

3-(2-Benzylthioethyl)indoles



Compd. No.	R	R′	Yield $^0/_0$	B. p. (range) ^{0}C/mm.[a]	M. p. ^{0}C	Formula	Analyses calc'd. found $^0/_0$ C	$^0/_0$ H	$^0/_0$ N	$^0/_0$ S
II	H	H	45	160—170/0.01	27—29[b]	$C_{17}H_{17}NS$	76.36 76.32	6.41 6.37	5.24 5.46	11.99 11.60
III	5-MeO	H	84	180—190/0.01	oil	$C_{18}H_{19}NOS$	72.69 72.77	6.44 6.55	4.71 4.91	10.78 10.84
IV	5-EtO	H	58	175—185/0.01	oil	$C_{19}H_{21}NOS$	73.27 73.36	6.80 6.88	4.50 4.48	10.30 10.02
V	5-PhCH$_2$O	H	77	—	63—65[c]	$C_{24}H_{23}NOS$	77.17 77.15	6.21 6.20	3.75 3.61	8.58 8.60
VI	7-MeO	H	53	150—160/0.005	oil	$C_{18}H_{19}NOS$	72.69 72.51	6.44 6.55	4.71 4.42	10.78 10.62
VII	H	Me	72	150—160/0.01	oil	$C_{18}H_{19}NS$	76.82 76.56	6.80 6.57	4.98 5.05	11.40 11.26

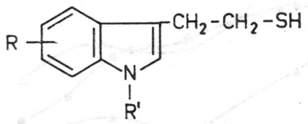
---

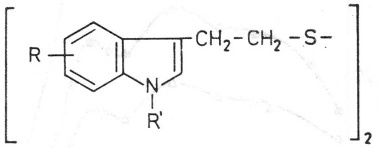
[a] microdistillation tube, Al-block temp; [b] from petroleumether; [c] from benzene-petroleumether.

formed on an equimolar scale in 25% acetic acid solution (ethanol-water 2 : 1) at 80°. After submitting the reaction products to alumina column chromatography thioethers II—VII were isolated in good yields as stable, mostly oily compounds (Table I).

The fact that the reaction succeeded also with the unsubstituted phenylhydrazine shows that the sulphur atom in the acetal moiety I enhances the relative ease of cyclization, and, unlike the acetals investigated previously[4], exerts a substantial effect on the formation and polarizability of the enhydrazine intermediate in the Fischer indole synthesis.

Debenzylation of thioethers II—VII with sodium in liquid ammonia resulted in the formation of the corresponding mercaptans (*A*) and disulphides (*B*). The products were separated successfully on alumina or silicagel columns. The thiols and disulphides on thin-layer chromatography were clearly differentiated with nitroprusside and Ehrlich reagent.





(*A*)			(*B*)
VIII	R = H	R′ = H	IX
X	= 5-MeO	= H	XI
XII	= 5-EtO	= H	XIII
XIV	= 5-OH	= H	XV
XVI	= 7-MeO	= H	XVII
XVIII	= H	= Me	XIX

It was observed that the ratio mercaptan—disulphide was shifting to the former compound when larger amounts of ammonium chloride were added during the debenzylation process, and when peroxide-free solvents were used during isolation. In pure state the mercaptans (*A*) are stable low-melting compounds, except the thiol analogs of 5-hydroxytryptophol and *N*-methyl tryptophol, XIV and XVIII respectively, which are fairly stable viscous oils; the melting points of the corresponding disulphides (*B*), with exception of the oily XIX, are considerably higher.

The infrared spectra of the prepared compounds agree well with the proposed structure. In the solid state (KBr pellets) the mercaptans showed the characteristic SH-stretching mode band of various intensities at about 2550 cm^{-1}; however, with VIII this absorption was visible only in carbon tetrachloride. In order to ascertain their thiolic structure, VIII, XIV and XVIII were treated with 2,4-dinitrofluorobenzene; the corresponding dinitrophenylthio-derivatives VIIIa, XIVa and XVIIIa were obtained in high yield.

Ultraviolet spectra of the prepared thioethers, mercaptans and disulphides resemble closely to those of their parent tryptamines. This is in agreement with the finding[6] that in contrast to indolyl-2-thiother series, the UV absorptions of indolyl-3-thioethers are practically indistinguishable from those of their

S-free parent indoles. However, because of different sulphur linkages the intensity of absorption differs considerably (Fig. 1); in the spectra of sulphur analogs of tryptophol the increase in the order: mercaptan, thioether, disulphide is evident.

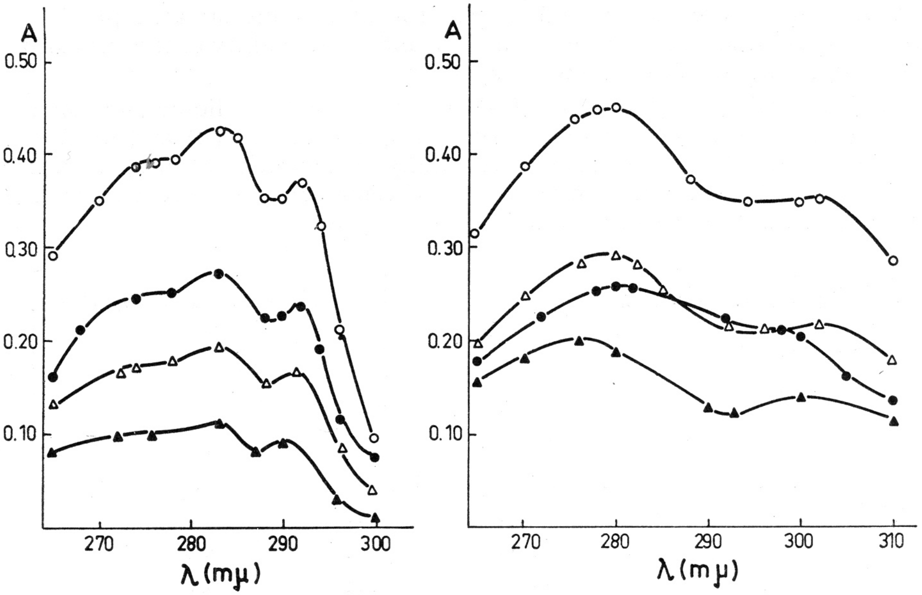


Fig. 1. Ultraviolet absorption spectra of (4×10^{-5} *M* in 95% ethanol):

—○— *Bis*-[3-(2-thioethyl)indole] (IX)
—●— 3-(2-Benzylthioethyl)indole (II)
—△— 3-(2-Mercaptoethyl)indole (VIII)
—▲— Tryptamine

—○— *Bis*-[5-Hydroxy-3-(2-thioethyl)indole] (XV)
—△— 5-Hydroxy-3-(2-mercaptoethyl)indole (XIV)
—●— 5-Benzyloxy-3-(2-benzylthioethyl)indole (V)
—▲— 5-Hydroxytryptamine

EXPERIMENTAL

Materials and Methods

Melting points are uncorrected. The IR spectra, unless stated otherwise, were determined on a Perkin-Elmer 137 infracord spectrophotometer. The UV spectra were measured in ethanol solutions (10^{-4} mole/l.) on a Beckman D. U. G. 2400 spectrophotometer. Thin-layer chromatography (TLC) was done on chromatoplates of silicagel G (Merck) in: 1. petroleum ether—benzene—methanol (20 : 15 : 2) and 2. chloroform—methanol (10 : 1). The spots were developed with: a) Ehrlich reagent (2% *p*-dimethylaminobenzaldehyde in 5% hydrochloric acid), b) nitroprusside reagent[12], c) iodo-platinate reagent[12], d) 10% sulphuric acid, e) iodine vapour. Paper chromatography, descending, one-dimensional was performed on Whatman No. 1 paper in: A. *n*-butanol—acetic acid—water (4 : 1 : 2), B. *iso*-propanol—ammonia—water (10 : 1 : 1), C. methanol—water (95 : 5).

p-*Methoxyphenylhydrazine Hydrochloride*. The free base, prepared by the procedure of Blaikie and Perkin[13] from *p*-anisidine, was dissolved in anhydrous benzene and a solution of dry HCl in anhydrous ether was added dropwise until the neutralization point was reached (excess of acid causes a blue coloration and degradation of the compound). The precipitated hydrochloride was filtered off, washed with ether and dried in a desiccator; yield: 48% (calc'd. on *p*-anisidine), m. p. $156—157^{0}$. One recrystallisation from ethanol—ether gave an analytically pure sample, m. p. $158—159^{0}$ (decomp.); Stroh[14] gives m. p. 169^{0} without experimental data.

4-Benzylthiobutanal diethyl acetal (I)

To vinylethanal diethyl acetal[15] (6.0 g., 41.6 mmoles) two drops of piperidine and freshly distilled benzyl mercaptan (5.2 g., 41.9 mmoles) were added under shaking and cooling in an ice bath, and the mixture kept under anhydrous conditions at 70—80° for 3 hours. After cooling, ether (30 ml.) was added, the solution washed with water, dried over K_2CO_3 and the solvent evaporated *in vacuo*. The remaining oil was distilled in high *vacuo*; yield: 7.9 g., 71% of I, b. p. 119—124°/0.01 mm. For analysis the oil was redistilled: b. p. 123—124°/0.01 mm.

Anal. $C_{15}H_{24}O_2S$ (268.40) calc'd.: C 67.12; H 9.01; S 11.95%
found: C 67.33; H 9.11; S 11.78%

3-(2-Benzylthioethyl)indoles II—VII. *General Procedure*

To a stirred solution of the corresponding phenylhydrazine hydrochloride (10 mmoles) in 90 ml. acetic acid—water—ethanol (25 : 25 : 40, by vol.), the equimolar amount of I (2.69 g.) dissolved in 10 ml. of ethanol was added dropwise at 80°. The heating and stirring was continued for 3 hours whereupon the reaction mixture was concentrated *in vacuo* to about one-third of the volume, and the separated oil extracted with benzene. The extracts were washed with sodium hydrogen carbonate solution and water, and dried over sodium sulphate. After the removal of the solvent, the oily residue was chromatographed on an alumina (Merck, neutral, 50 g.) column packed with petroleum ether. The elution was performed successively with: petroleum ether, petroleum ether—benzene (3 : 1), (2 : 1), (1 : 1), and benzene, the displacement of the products being followed by TLC in solvent 1. with Ehrlich reagent. In some cases still impure fractions were submitted to a second alumina chromatography. Chromatographically pure fractions were then combined, evaporated to dryness, and the oily residue used in the next step of the reaction. For analysis a sample was submitted either to distillation or to crystallisation. The yields and analytical data of thioethers II—VII are given in Table I.

IR spectra of II—VII showed absorption at 3350—3400 s (indolic NH), 2850—2920 m (CH_2), 1480—1630 (three peaks m and s, aromatic conjugation), 705 s (monosubstituted benzene) and 750—765 cm^{-1} m (3-substituted indoles).

On paper chromatograhy II—VII are practically indistinguishable in solvent A ($R_f \sim 0.95$), B ($R_f \sim 0.90$), and C ($R_f \sim 0.75$): positive reaction with iodo-platinate reagent; Ehrlich reagent: II—V blue spot, VI—VII blue-brown, very weak (vw), after heating.

Debenzylation of 3-(2-benzylthioethyl)indoles II—VII. *General Procedure*

To 5—7 mmoles of the corresponding thioether dissolved in about 5 ml. of anhydrous ether, dry ammonia (60—100 ml.) was added, and sodium (6—8 mgatom per mmole of benzyl group) was added under stirring at — 40° over half an hour. The resulting blue solution was stirred for an additional half hour, whereupon ammonium chloride, equivalent to the sodium used, was gradually added. Ammonia was evaporated by a stream of nitrogen and last traces were removed by keeping the mixture in a vacuum desiccator over sulphuric acid. To the residue water was added (30—60 ml., boiled and cooled immediately before use), the mixture was adjusted with 2*N* HCl to *p*H 5 and extracted with peroxide-free ether. The combined extracts were washed with water, dried over sodium sulphate, the solvent was removed *in vacuo,* and the remaining mixture submitted to column chromatography. Debenzylation products of II, III, IV and VI were purified on an alumina (30—40 g.) column packed with petroleum ether and eluted subsequently with: petroleum ether, petroleum ether—benzene (2 : 1), (1 : 1), benzene, benzene—chloroform (1 : 1), chloroform and chloroform—acetone (1 : 1). In all cases dibenzyl was eluted as the first compound. The displacement of indoles was followed by TLC in solvent 1. if not stated otherwise. Thiols VIII, X, XII, XIV and XVI gave with Ehrlich reagent a yellow spot which turned green and finally blue, while their corresponding disulphides gave a reddish spot which changed to blue-violet.

On paper chromatography all the thiols and disulphides (VIII—XIX) gave positive test with iodo-platinate reagent; colours obtained with Ehrlich reagent are given with each particular compound. In solvent B the thiols underwent a partial or complete oxidation to the corresponding disulphide.

3-(2-Mercaptoethyl)indole (VIII) *and* bis-[*3-(2-Thioethyl)indole*] (IX)

The thiol VIII was eluted with petroleum ether—benzene (2 : 1) as on oil with crystallised on standing, yield 47%. For analysis it was crystallised from petroleum ether; m. p. 43—44.5°. IR spectrum (in CCl_4, Perkin Elmer Model 221): 3385 s (NH), 2570 w (SH), 750 cm^{-1} s (3-substituted indole). R_f values: *A* 0.95, and C 0.79 (vw yellow brown spot), B 0.91 (vw reddish-grey).

Anal. $C_{10}H_{11}NS$ (177.26) calc'd.: C 67.76; H 6.25; N 7.90; S 18.09%
found: C 68.03; H 6.18; N 7.93; S 17.86%

The disulphide IX was eluted with chloroform-acetone (1 : 1) in a 27% yield; white crystals from benzene, m. p. 119—120°. IR spectrum (KBr): 3390 s (NH), 750 cm^{-1} s (3-substituted indole). R_f values: A 0.96, B 0.94, C 0.56 (vw reddish-grey).

Anal. $C_{20}H_{20}N_2S_2$ (352.51) calc'd.: C 68.14; H 5.72; N 7.95; S 18.19%
found: C 67.85; H 5.97; N 8.12; S 18.08%

3-[2-(2',4'-Dinitro)phenylthioethyl] indole (VIIIa)

To a solution of VIII (80 mg., 0.452 mmoles) in 2 ml. ethanol, an equimolar amount of sodium hydrogen carbonate (36 mg.) in 1 ml. water and 2,4-dinitrofluorobenzene (79 mg.) in 1 ml. of ethanol were added. The mixture was shaken at room temperature for 1.5 hour, and the precipitate filtered off; yield 150 mg. (100%) of yellow crystals, m. p. 188—191°. Recrystallised from chloroform, m. p. 190.5—192°.

Anal. $C_{16}H_{13}N_3O_4S$ (343.34) calc'd.: C 55.97; H 3.81; N 12.24; S 9.34%
found: C 55.71; H 4.06; N 12.49; S 9.37%

5-Methoxy-3-(2-mercaptoethyl)indole (X) *and* bis-[*5-Methoxy-3--(2-thioethyl)indole*] (XI)

Elution with petroleum ether—benzene (2 : 1) and (1 : 1) gave X, yield 49%. For analysis it was crystallised from petroleum ether; m. p. 45—46°. IR spectrum (KBr): 3360 s (NH), 2560 cm^{-1} m (SH). R_f values: A 0.93 and C 0.77 (yellow → greenish--blue), B 0.88 (reddish → blue).

Anal. $C_{11}H_{13}NOS$ (207.29) calc'd.: C 63.73; H 6.32; N 6.76; S 15.47%
found: C 63.49; H 6.44; N 7.02; S 15.24%

Further elution of the column with benzene and benzene—chloroform (1 : 1) gave XI; white crystals (13%) from benzene—petroleum ether, m. p. 90.5—91.5°. IR spectrum (KBr): 3390 cm^{-1} s (NH). R_f values: A 0.96, B 0.88, C 0.66 (reddish → blue).

Anal. $C_{22}H_{24}N_2O_2S_2$ (412.56) calc'd.: C 64.04; H 5.86; N 6.79; S 15.55%
found: C 64.01; H 6.11; N 7.06; S 15.87%

5-Ethoxy-3-(2-mercaptoethyl)indole (XII) *and* bis-[*Ethoxy-3--(2-thioethyl)indole*] (XIII)

The thiol XII was eluted with petroleum ether—benzene in 66% yield. The oil was dissolved in benzene and petroleum ether was added subsequently; after 2 days white crystals (46%) of XII, m. p. 44—46° separated. IR spectrum (KBr): 3400 s (NH), 2580 cm^{-1} w (SH). R_f values: A 0.93 and C 0.78 (yellow → blue), B 0.89 (reddish → blue).

Anal. $C_{12}H_{15}NOS$ (221.31) calc'd.: C 65.12; H 6.83; N 6.33; S 14.49%
found: C 65.14; H 6.78; N 6.56; S 14.30%

Elution with benzene-chloroform (1 : 1) gave XIII in 24% yield; it was crystallised from chloroform—petroleum ether, m. p. 82—83°. IR spectrum (KBr): 3400 cm^{-1} s (NH). R_f *values:* A 0.94, B 0.90, C 0.69 (reddish → blue).

Anal. $C_{24}H_{28}N_2O_2S_2$ (440.61) calc'd.: C 65.42; H 6.41; N 6.36; S 14.56%
found: C 65.27; H 6.14; N 6.65; S 14.39%

5-Hydroxy-3-(2-mercaptoethyl)indole (XIV) *and* bis-[*5-Hydroxy-3--(2-thioethyl)indole*] (XV)

The crude debenzylation product was dissolved in a minimum amount of peroxide-free ether, benzene was added till turbidity, and the solution was put on a silicagel column (Merck, 0.2—0.5 mm., 20 g.) packed with benzene. The elution was performed subsequently with: benzene, chloroform and chloroform-peroxide free ether (5 : 1), the emergence of the products being followed by TLC in solvent 2. The thiol XIV was displaced with the last solvent as a yellow oil in 61% yield, followed by the crystalline disulphide XV. After elution the column turned dark brown.

Attempts to bring XIV to crystallisation failed. For analysis the oil was purified on a second silicagel column packed with benzene and eluted with benzene and chloroform; the latter solvent displaced XIV as a light yellow oil which was analytically pure. IR spectrum (neat): 3350 vs (NH, OH), 2520 cm^{-1} w (SH). R$_f$ values: A 0.90 and C 0.75 (yellow → blue), B 0.84 (reddish → blue).

Anal. $C_{10}H_{11}NOS$ (193.26) calc'd.: C 62.14; H 5.74; N 7.25; S 16.59%
found: C 61.88; H 5.72; N 7.01; S 16.39%

An analytically pure sample kept in a stoppered vial in darkness for six months showed on TLC only traces of the corresponding disulphide, although its colour changed to yellow-brown.

The disulphide XV, obtained in 16% yield was recrystallised from benzene and then from chloroform; m. p. 132—134° (softening at 120°). IR spectrum (KBr): 3500 m, 3340 cm^{-1} s (OH, NH). R$_f$ values: A 0.93, B 0.88, C 0.68 (reddish → violet).

Anal. $C_{20}H_{20}N_2O_2S_2$ (384.51) calc'd.: C 62.47; H 5.24; N 7.29; S 16.68%
found: C 62.79; H 5.04; N 7.48; S 16.72%

5-Hydroxy-3-[2-(2',4'-dinitro)phenylthioethyl]indole (XIVa)

Prepared in a quantitative yield from the thiol XIV in the same way as described for VIIIa; brick-red crystals, m. p. 222—224°. For analysis they were recrystallised from a large quantity of methanol, m. p. 226—228°. IR spectrum (KBr): 3500 m, 3350 cm^{-1} s (OH, NH).

Anal. $C_{16}H_{13}N_3O_5S$ (359.35) calc'd.: C 53.47; H 3.65; N 11.69; S 8.92%
found: C 53.52; H 3.55; N 11.80; S 9.14%

7-Methoxy-3-(2-mercaptoethyl)indole (XVI) *and* bis-[*7-Methoxy-3-(2-thioethyl)-indole*] (XVII)

The thiol XVI was eluted with petroleum ether; after crystallisation from benzene—petroleum ether 57% of crystals, m. p. 70—73° were obtained. Recrystallised from petroleum ether; m. p. 72—74°. IR spectrum (KBr, Perkin Elmer Model 221): 3420 s (NH), 2570 w (SH). R$_f$ values: A 0.95 and C 0.75 (yellow → blue), B 0.89 (vw blue-brown, after heating).

Anal. $C_{11}H_{13}NOS$ (207.29) calc'd.: C 63.73; H 6.32; N 6.76; S 15.47%
found: C 63.75; H 6.42; N 6.94; S 15.79%

Elution with benzene afforded 19% of crystalline disulphide XVII. It was recrystallised from benzene—petroleum ether; m. p. 108—110°. IR spectrum (KBr): 3420 cm^{-1} s (NH). R$_f$ values: A 0.95, B 0.89, C 0.64 (vw blue-brown, after heating).

Anal. $C_{22}H_{24}N_2O_2S_2$ (412.56) calc'd.: C 64.04; H 5.86; N 6.79; S 15.55%
found: C 64.17; H 5.97; N 6.78; S 15.63%

1-Methyl-3-(2-mercaptoethyl)indole (XVIII) *and* bis-[*1-Methyl-3--(2-thioethyl)indole*] (XIX)

The crude debenzylation product was dissolved in a minimum amount of petroleum ether—benzene (3 : 1), put on a silicagel column and eluted with the same solvent. After displacement of dibenzyl, XIX emerged as a colourless oil which gave on TLC a red → blue spot with Ehrlich reagent and a positive test on SH group; yield: 58%. For analysis it was distilled at 100—110°/10 μ (Al block). IR spectrum (neat): 2580 cm⁻¹ w (SH). R_f values: A 0.95, B 0.88, C 0.81 (vw blue, after heating).

Anal. $C_{11}H_{13}NS$ (191.28) calc'd.: C 69,07; H 6.85; N 7.32; S 16.76%
found: C 68.93; H 6.69; N 7.59; S 16.83%

Further elution with petroleum ether—benzene (1 : 1) displaced XIX (23 mg., 2.3%) as an oil which was rechromatographed on a silicagel column with the same solvent. R_f values: A 0.96, B 0.89, C 0.64 (no visible colour with Ehrlich reagent).

Anal. $C_{22}H_{24}N_2S_2$ (380.56) calc'd.: C 69.43; H 6.36; N 7.36; S 16.85%
found: C 69.19; H 6.51; N 7.50; S 17.10%

1-Methyl-3-[2-(2',4'-dinitro)phenylthioethyl]indole (XIXa)

Prepared from XIX as described for VIIIa; yellow crystals yield 98%, m. p. 194—197°. For analysis it was recrystallised from acetone; m. p. 207—209°.

Anal. $C_{17}H_{15}N_3O_4S$ (357.38) calc'd.: C 57.13; H 4.23; N 11.76; S 8.97%
found: C 56.95; H 4.44; N 11.51; S 8.77%

Acknowledgment. The authors are indebted to Dr. O. Hadžija nad Miss N. Horvatić for the microanalyses.

REFERENCES

1. D. Keglević, N. Stojanac, and D. Desaty, *Croat. Chem. Acta* **33** (1961) 83.
2. D. Desaty, O. Hadžija, S. Iskrić, D. Keglević, and S. Kveder, *Biochim. Biophys. Acta* **62** (1962) 179.
3. D. Desaty and D. Keglević, *Croat. Chem. Acta* **36** (1964) 103.
4. D. Desaty and D. Keglević, *Croat. Chem. Acta* **37** (1965) 25.
5. Th. Wieland and D. Grimm, *Chem. Ber.* **98** (1965) 1727.
6. Th. Wieland and K. Rühl, *Chem. Ber.* **96** (1963) 260.
7. R. V. Jardine and R. K. Brown, *Can. J. Chem.* **43** (1965) 1293.
8. E. Piers, V. B. Haarstad, R. J. Cushley, and R. K. Brown *Can. J. Chem.* **40** (1962) 511.
9. J. K. Horner and W. A. Skinner, *Can. J. Chem.* **42** (1964) 2904.
10. J. K. Horner, J. I. DeGraw, and W. A. Skinner, *Can. J. Chem.* **44** (1966) 307.
11. M. S. Grant and H. R. Snyder, *J. Am. Chem. Soc.* **82** (1960) 2742.
12. I. M. Hais and K. Macek, editors, *Handbuch der Papierchromatographie*, Vol. I, G. Fischer-Verlag, Jena, 1958, p. 761 and p. 748.
13. K. G. Blaikie and W. H. Perkin, Jr., *J. Chem. Soc.* **125** (1924) 296.
14. H. H. Stroh, *Chem. Ber.* **91** (1958) 2645.
15. R. I. Hoaglin, D. G. Kubler, and A. E. Montagna, *J. Am. Chem. Soc.* **80** (1958) 5460.

IZVOD

Indolski spojevi. V. 3-(2-Merkaptoetil)indoli i *bis*-[3-(2-tioetil)indoli], sumporni analogoni triptofola, 5-hidroksitriptofola i drugih *Bz*-supstituiranih triptofola

D. Keglević, D. Desaty, D. Goleš i L. Stančić

Opisana je jednostepena ciklizacija 4-benziltioetilbutanal dietil acetala s različitim fenilhidrazin hidrokloridima u 3-(2-benziltioetil)indole, pod blagim reakcionim uvjetima. Debenzilacijom tih spojeva s natrijem u tekućem amonijaku dobiveni su odgovarajući 3-(2-merkaptoetil)indoli i *bis*-[3-(2-tioetil)indoli], sumporni analogoni triptofola.

TRACER LABORATORIJ
INSTITUT »RUĐER BOŠKOVIĆ«
ZAGREB

Primljeno 3. studenoga 1967.