Table 1 (*Contd*)

| $P$ atm | $\rho$ moles litre$^{-1}$ | $C_{exp}$ ms$^{-1}$ | $C_{calc}$ ms$^{-1}$ | $\Delta\mu$% |
|---|---|---|---|---|
| $T$ = 245.055 K | | | | |
| 27.22 | 17.455 | 396.10 | 487.06 | 18.67 |
| 34.02 | 17.576 | 403.51 | 505.97 | 20.25 |
| 40 83 | 17.675 | 410 48 | 524.43 | 21.73 |
| 47.63 | 17.768 | 417.07 | 545.63 | 23.56 |
| 54.44 | 17.856 | 423.31 | 564.67 | 25.03 |
| 61.24 | 17.934 | 429.25 | 586.94 | 26.87 |
| $T$ = 255.094 K | | | | |
| 27.22 | 16.486 | 347.74 | 461.16 | 24.59 |
| 34.02 | 16.629 | 358.18 | 481.88 | 25.67 |
| 40.83 | 16.774 | 367.68 | 501.09 | 26.61 |
| 47.63 | 16.912 | 376.30 | 519.08 | 27.50 |
| 54.44 | 17.031 | 384.41 | 539.11 | 28.69 |
| 61.24 | 17.140 | 391.86 | 560.96 | 30.14 |
| $T$ = 265.144 K | | | | |
| 34.02 | 15.646 | 300.63 | 414.31 | 27.44 |
| 40.83 | 15.842 | 315.66 | 446.50 | 29.30 |
| 47.63 | 16.040 | 328.51 | 480.58 | 31.64 |
| 54.44 | 16.211 | 339.80 | 539.96 | 37.07 |
| $T$ = 275.239 K | | | | |
| 47.63 | 14.528 | 264.68 | 351.46 | 24.69 |
| 54.44 | 14.817 | 284.28 | 386.77 | 26.37 |
| 61.24 | 15.098 | 300.00 | 420.17 | 28.61 |

increase in the density of the liquid xenon. At higher temperature and pressure, the percentage deviation is greater than that at lower temperature and pressure.

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## SYNTHESIS OF VARIOUS *BIS*-1,3,4-OXADIAZOLYL, *BIS*-1,3,4-THIADIAZOLYL AND *BIS*-1,3,4-TRIAZOLYL COMPOUNDS

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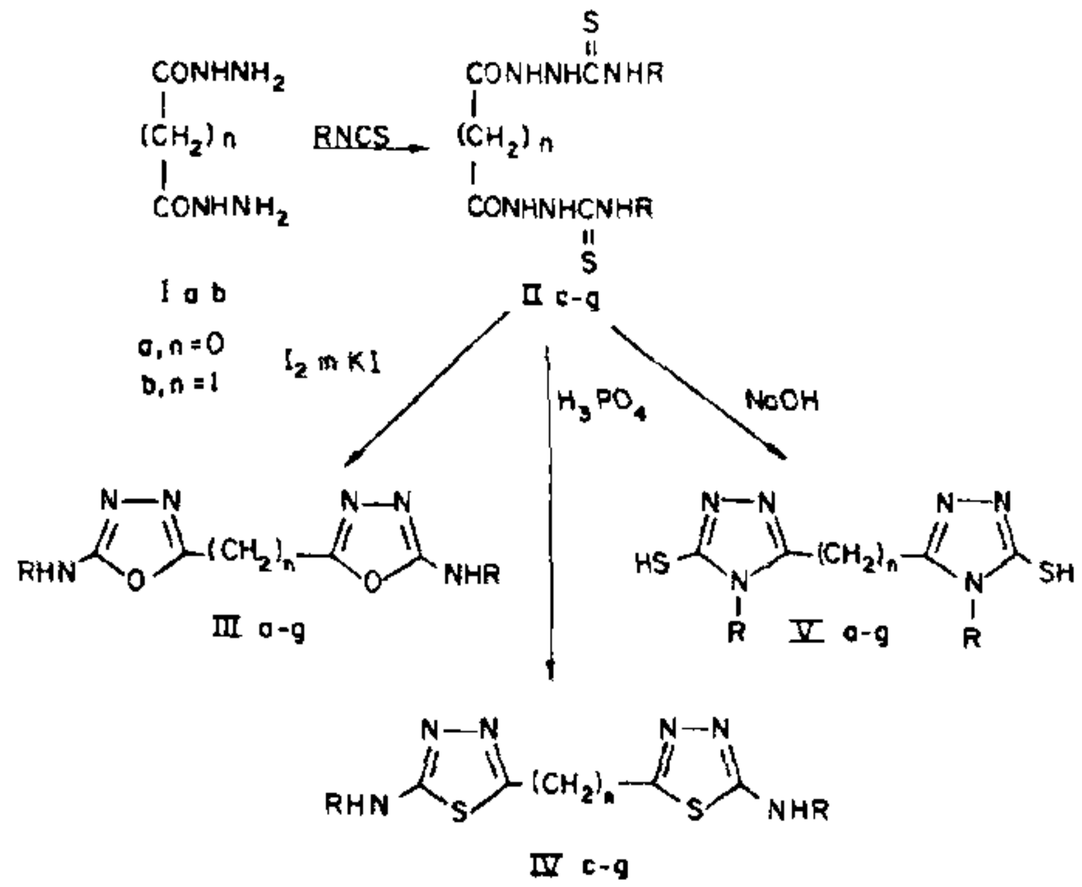
COMPOUNDS containing triazole and thiadiazole ring are known to possess fungicidal,[1,2] pesticidal,[3] insecticidal[4], bactericidal[5] and antiinflammatory[6] activities. Some *bis* heterocycles[7] have recently been reported to display fungicidal activity. We now report the synthesis of various substituted *bis*-1,3,4-oxadiazolyl, *bis*-1,3,4-thiadiazolyl and *bis*-1,3,4-triazolyl compounds.

The oxalyl/malonyl hydrazides (Ia–b) reacted with methyl, allyl, phenyl, *p*-tolyl, *p*-anisyl and *p*-chlorophenyl isothiocyanates to yield thiosemicarbazides (IIa–g) in quantitative yields. The IR spectra of IIIa–g with bands in the region 3200–3350 (NH), 1680 (C=O) and 1110 cm$^{-1}$ (C=S) were compatible with the structure.

The oxidative cyclization of IIa–g by reacting with iodine in potassium iodide gave *bis*-(5-alkyl/arylamino-1,3,4-oxadiazol-2-yl)alkanes (IIIa–g), (scheme 1).

The acid-catalysed cyclodehydration of thiosemicarbazides (IIa–b) using anhydrous orthophosphoric acid was not satisfactory and the expected *bis*-(5-alkylamino-1,3,4-thiadiazol-2-yl)alkanes (IVa–b) could not be isolated. However similar cyclisation of IIc–g led to the formation of *bis*-(5-arylamino-1,3,4-thiadiazol-2-yl)alkanes in good yields (scheme 1). The absence of carbonyl absorption band and appearance of strong absorption peak in the region of 1620 (C=N) along with a band at 3300 cm$^{-1}$ (NH) in the IR spectra




Scheme-1

| | n | R | | n | R |
|---|---|---|---|---|---|
| a, | 0 | $CH_3$ | e | 0 | $C_6H_4OCH_3$ |
| b, | 0 | $CH=CH_2$ | f | 0 | $C_6H_4Cl$ |
| c, | 0 | $C_6H_5$ | g | 1 | $C_6H_5$ |
| d, | 0 | $C_6H_4CH_3$ | | | |

of IIIa–g and IVc–g confirmed the anticipated ring closure.

Base-catalysed cyclodehydration of IIa–g using 4% aqueous sodium hydroxide gave the respective *bis*-(1-alkyl/arylamino-5-mercapto-1,3,4-triazol-2-yl) alkanes (Va–g). IR spectra of triazoles exhibited an absorption band at 1610 $cm^{-1}$ (C=N) and all other characteristic absorption bands due to conjugated cyclic system.

The biological screening of these compounds is in progress.

**Table 1** *Physical Data of Oxalyl/Malonyl Thiosemicarbazides*

| Comp. No. | R | *n* | M.P. °C | Yield % | Molecular formula |
|---|---|---|---|---|---|
| IIa | Methyl | O | 205(d) | 85.3 | $C_6H_{12}N_6O_2S_2$ |
| IIb | Allyl | O | 197(d) | 80.0 | $C_8H_{12}N_6O_2S_2$ |
| IIc | Phenyl | O | 158 | 88.2 | $C_{16}H_{16}N_6O_2S_2$ |
| IId | *p*-Tolyl | O | 184 | 79.0 | $C_{18}H_{20}N_6O_2S_2$ |
| IIe | *p*-Anisyl | O | 200 | 84.0 | $C_{18}H_{20}N_6O_4S_2$ |
| IIf | *p*-Chlorophenyl | O | > 295 | 81.0 | $C_{16}H_{14}N_6O_2S_2Cl_2$ |
| IIg | Phenyl | 1 | 186 | 79.5 | $C_{17}H_{18}N_6O_2S_2$ |

**Table 2** *Physical data of various compounds synthesized*

| Comp. No. | R | *n* | M.P. °C | Yield % | Molecular formula |
|---|---|---|---|---|---|
| IIIa | Methyl | 0 | > 250 | 62.1 | $C_6H_8N_6O_2$ |
| IIIb | Allyl | 0 | > 250(d) | 55.0 | $C_8H_8N_6O_2$ |
| IIIc | Phenyl | 0 | 319 | 65.0 | $C_{16}H_{12}N_6O_2$ |
| IIId | *p*-Tolyl | 0 | 275–6 | 62.8 | $C_{18}H_{16}N_6O_2$ |
| IIIe | *P*-Anisyl | 0 | 283(d) | 64.3 | $C_{18}H_{16}N_6O_4$ |
| IIIf | *p*-Chlorophenyl | 0 | 266(d) | 60.8 | $C_{16}H_{10}N_6O_2Cl_2$ |
| IIIg | Phenyl | 1 | 115 | 62.5 | $C_{17}H_{14}N_6O_2$ |
| IVc | Phenyl | 0 | 260 | 85.1 | $C_{16}H_{12}N_6S_2$ |
| IVd | *p*-Tolyl | 0 | 270(d) | 83.0 | $C_{18}H_{16}N_6S_2$ |
| IVe | *p*-Anisyl | 0 | 203 | 86.5 | $C_{18}H_{16}N_6O_2S_2$ |
| IVf | *p*-Chlorophenyl | 0 | 207 | 85.2 | $C_{16}H_{10}N_6S_2Cl_2$ |
| IVg | Phenyl | 1 | 158 | 80.0 | $C_{17}H_{14}N_6S_2$ |
| Va | Methyl | 0 | 330(d) | 58.0 | $C_6H_8N_6S_2$ |
| Vb | Allyl | 0 | 266 | 49.0 | $C_8H_8N_6S_2$ |
| Vc | Phenyl | 0 | 303(d) | 75.1 | $C_{16}H_{12}N_6S_2$ |
| Vd | *p*-Tolyl | 0 | > 250 | 72.4 | $C_{18}H_{16}N_6S_2$ |
| Ve | *p*-Anisyl | 0 | 289 | 75.1 | $C_{18}H_{16}N_6O_2S_2$ |
| Vf | *p*-Chlorophenyl | 0 | > 250 | 70.9 | $C_{16}H_{10}N_6S_2Cl_2$ |
| Vg | Phenyl | 1 | 278 | 74.9 | $C_{17}H_{14}N_6S_2$ |

All compounds gave satisfactory C, H and N analyses. The results agreed with the calculated values within the limits of experimental error.

*Experimental Procedure*

Melting points were determined in capillaries and are uncorrected. The IR spectra were recorded in nujol on a Perkin-Elmer 297 IR spectrophotometer. All the compounds analysed satisfactorily for C, H and N.

*Preparation of thiosemicarbazides* (IIa–g)

A suspension of acid hydrazide Ia–b (0.05 mole) in rectified spirit (25 ml) was treated with appropriate isothiocyanate (0.1 mole) and heated under reflux for 2 hr. The thiosemicarbazide which separated was collected and crystallized from a suitable solvent (table 1).

*Bis-(5-alkyl arylamino-1,3,4-oxadiazole-2-yl)alkanes* (IIIa–g)

To a suspension of the foregoing thiosemicarbazide (0.005 mole) in rectified spirit (150 ml), was added aqueous sodium hydroxide (5 ml, 4N). To the clear solution thus obtained, $I_2$ in KI (aqueous; 5%) was added gradually with shaking till the colour of $I_2$ persisted at room temperature. The contents were refluxed for 45 min and more, iodine was added (if necessary till $I_2$ colour persisted). The separated solid was collected and crystallized from suitable solvent (table 2).

*Bis-(5-arylamino-1,3,4-thiadiazole-2-yl)alkanes* (IVc–g)

Thiosemicarbazide (0.005 mole) was added gradually to anhydrous orthophosphoric acid (20 ml) in about 30 min. The reaction mixture was then heated at 120–130° for 30 min in an oil bath. The resulting slurry was poured on to ice-cold water and stirred. The crude solid thus separated was collected and crystallized from a suitable solvent (table 2).

*Bis-(1-alkyl,arylamino-5-mercapto-1,3,4-triazole-2-yl)-alkanes* (Va–g)

Thiosemicarbazide (IIa–g) (0.005 mole) was heated under gentle reflux with aqueous sodium hydroxide (4%, 33 ml) for 1 hr. The clear solution after treatment with activated charcoal was filtered and cooled. The filtrate was acidified with acetic acid and crystallized from suitable solvent (table 2).

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## DIFFERENTIATION OF NEOHESPERIDOSE AND RUTINOSE BY CMR SPECTROSCOPY

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NEOHESPERIDOSE and rutinose are the two disaccharides made up of D-glucose and L-rhamnose and commonly found as part of phenolic glycosides[1] occurring in plants. Neohesperidose is 2-O-α-L-rhammopyranosyl β-D-glucopyranose and rutinose is 6-O-α-L rhamno pyranosyl β-D-glucopyranose. These isomers differ markedly in their ability to impart taste to the corresponding polyphenolic glycosides. Thus, flavanone neohesperidoside is associated with bitter taste and dihydro chalkone neohesperidoside with sweet taste, while the aglycone or sugar separately is tasteless. The rutinosides of flavanone and dihydrochalkone, on the other hand, are tasteless either in combination or in isolation.

The differentiation of these disaccharides differing only in the position of inter linkage can be made by the conventional method of permethylation, hydrolysis and identification[2] of the tri-O-methyl glucose, if sufficient material is available. In the case of poor yield of the glycoside which is common in flavonoid derivatives from plants, $^1$H NMR has been employed[3] to characterize them making use of the difference in the absorption frequency of the anomeric proton ($H_1$, $\delta \approx 4.95$, *d*, J = 2Hz) and $CH_3$ ($\delta \approx 1.2$, *d*, J = 6Hz) of rhamnose in neohesperidoside from that ($H_1$, $\delta \approx 4.3$, *d*, J = 2Hz; $CH_3$, $\delta \approx 0.85$, broad *m*) in rutinoside. However, it has been found difficult to elicit