

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-aryl amino-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 glycosides¹ occurring in plants. Neohesperidose is 2-O- α -L-rhamnopyranosyl 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 rutinoides of flavanone and dihydro-chalkone, 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 identification² 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, ¹H NMR has been employed³ to characterize them making use of the difference in the absorption frequency of the anomeric proton (H_1 , $\delta \approx 4.95$, d , $J = 2\text{Hz}$) and CH_3 ($\delta \approx 1.2$, d , $J = 6\text{Hz}$) of rhamnose in neohesperidoside from that (H_1 , $\delta \approx 4.3$, d , $J = 2\text{Hz}$; CH_3 , $\delta \approx 0.85$, broad m) in rutinoides. However, it has been found difficult to elicit

reliable correlation by ^1H NMR alone and is most useful in combination with ^{13}C NMR (CMR) data^{4,5}.

The CMR spectrum of the disaccharides in DMSO-d_6 reveals significant difference in the absorption frequency of C_2 and C_6 of glucose and C_6 of rhamnose (C_6) in neohesperidose ($\text{C}_2: \delta \approx 77.3$; $\text{C}_6 \approx 61$; $\text{C}_6' \approx 20.9$) and rutinose ($\text{C}_2 \approx 73.5$; $\text{C}_6 \approx 66.5$; $\text{C}_6' \approx 18$). There is no record of CMR spectra of acetyl derivatives of neohesperidosides, though the preparation is easy and the acetate can be dissolved in less costly CDCl_3 for the spectral measurements. In view of this and as part of our work in determining the nature of the disaccharide of a new natural product⁶, we obtained the CMR spectra of peracetate of scutellarein 7-rhamno glucoside and peracetate of naringin (a neohesperidoside) and compared with the spectrum⁷ of peracetate of diosmin (a rutinoside). These spectra gave evidence that the absorption frequency of C_2 and C_6 of glucose in peracetate of neohesperidose ($\text{C}_2 \approx 71.2$; $\text{C}_6 \approx 62.2$) and rutinose ($\text{C}_2 \approx 72.4$; $\text{C}_6 \approx 66.2$) were comparable with those in the underivatized compounds (after allowing shift⁸ due to OAc group) where as the frequency of the rhamnose CH_3 (C_6') was found to be considerably increased (δ , 17.50) in neohesperidoside and very close to that (δ , 17.60) in rutinoside; the assignment of the signal confirmed by the peak multiplicity (q). The upfield shift of C_6 of rhamnose in peracetate of neohesperidoside is unexplainable as there is no acetyl group attached to its ortho carbon. There is, as expected, no difference in the frequency of C_6 of rhamnose in peracetate of rutinose. The frequency of C_6 of rhamnose in naringin (δ , 17.8), reported recently⁹ is same as that in peracetate. Thus, in CMR differentiation of neohesperidoside and rutinoside reliance can be placed on the frequency of C_2 and C_6 of glucose and not on C_6 of rhamnose. The CMR spectrum of the disaccharide in DMSO-d_6 or that of its peracetate in CDCl_3 is of equal utility and hence the latter is considered preferable from economic point of view.

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MINI COLUMNAR JOINTS IN BASALTS, OF KODALI VILLAGE, MAHARASHTRA.

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MINI Columnar Joints are exposed in Basalts West of Kodali village (North Latitude $15^\circ 47' 30''$ and East Longitude $74^\circ 10' 40''$). Columnar joints have got exposed during excavation connected with the Tilari hydroelectric dam project.

The basalts belong to Deccan trap period and consist of massive compact flows followed by basalts showing columnar joints. The columnar basalt is about 1 m thick and extends over an exposed length of about 30 m. The most striking character is the development of countless vertical small columns, unlike the more common wide columns described in literature like the Giant's Causeway Co. Antrim, Fingal's Cave Island Staff, St. Mary Island off Malpe Coast, Karnataka, and Andheri Columnar basalts, Bombay. The vertical columns are broken up by many horizontal cross joints. Each column is 1 cm wide. As far as the authors are aware such fine columnar joints have not been so far reported from the Deccan basalt terrain and hence attention is drawn to this occurrence.