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NOTE

Mass spectral studies of 6-substituted-2-methylthio-9-tetrahydrofuranylpurine nucleoside analogues

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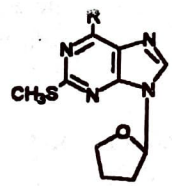
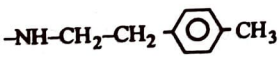
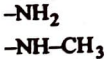
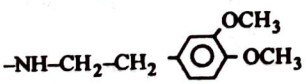
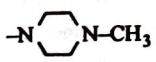
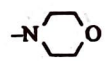
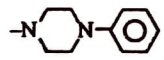
The mass fragmentation studies of eight compounds of the series 6-substituted-2-methylthio-9-tetrahydrofuranylpurine (1-8) have been carried out. Two types of fragmentation pattern is observed depending on the amino function. The details are reported as model of purine deoxy nucleosides.

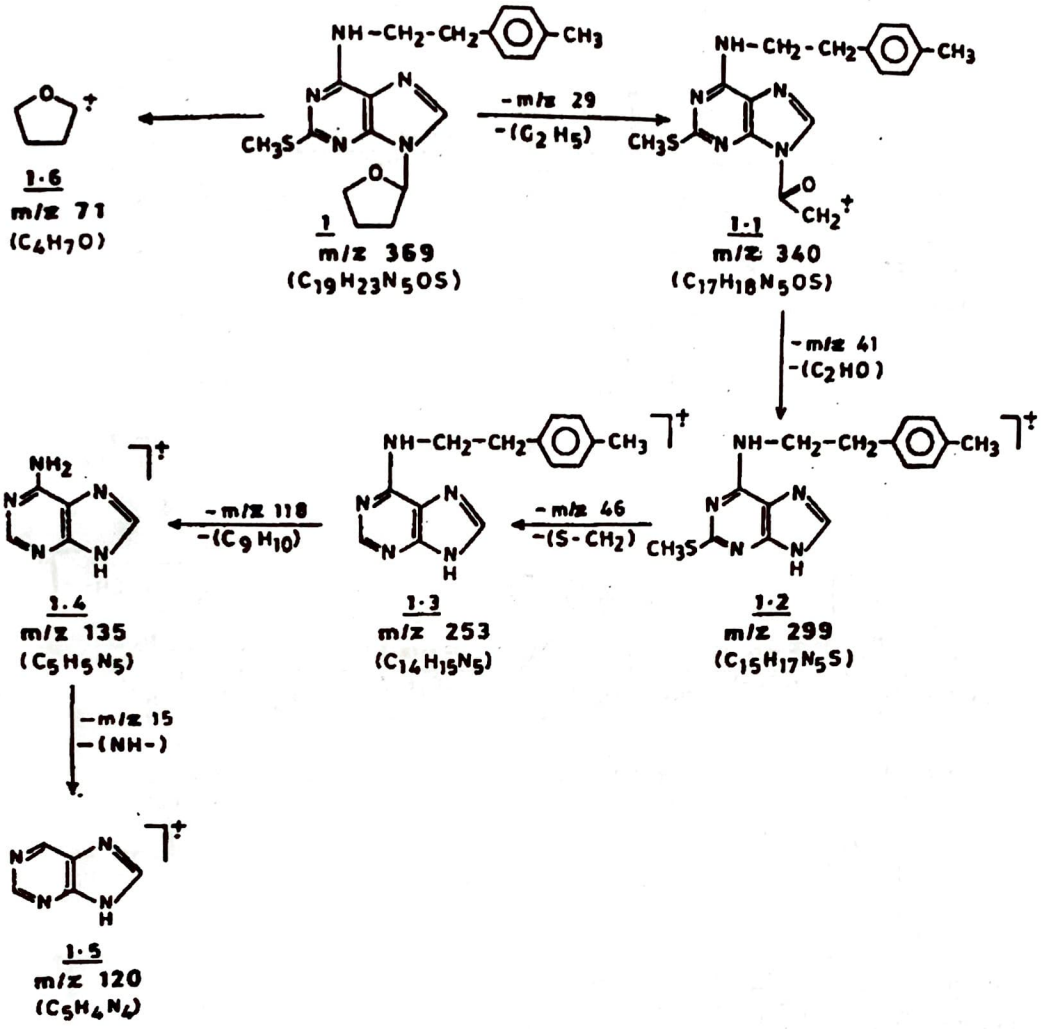
The compounds of the series of 6-substituted-2-methylthio-9-tetrahydrofuranylpurine (**1-8**) have been synthesized by known methods[1], and evaluated for antiviral activity which will be reported later. The mass spectra of these compounds were analysed in detail using EI technique and a consistent fragmentation pattern has been observed[2]. The various peaks observed are given in Table 1.

The general fragmentation pattern indicates the rearrangement in tetrahydrofuran moiety leading to the cleavage of C–N bond between the purine and tetrahydrofuran. All the compounds analysed exhibited a fragmentation peak at (M^+-71). Some variations in the fragmentation patterns were observed among the compounds having secondary amino (**1-4**) and those having tertiary amino (**5-8**) functions at position-6. In the compounds **1-4**, the next peak formed was by the loss of 46 units corresponding to the loss of CH_2-S group. The next point of fragmentation was the amino group which fragmented to give peak at *m/z* 135 assigned to 6-

Table 1



Compd. no.	R	M^+	*m/z*
1		369	340, 299, 253, 135, 120, 71
2		251	222, 181, 135, 120, 71
3		265	236, 195, 148, 135, 120, 71
4		415	386, 345, 301, 135, 120, 71
5		334	305, 264, 230, 207, 193, 166, 120, 71
6		319	290, 249, 207, 203, 193, 166, 120, 71
7		321	292, 251, 205, 207, 193, 166, 120, 71
8		396	367, 326, 206, 193, 166, 120, 71



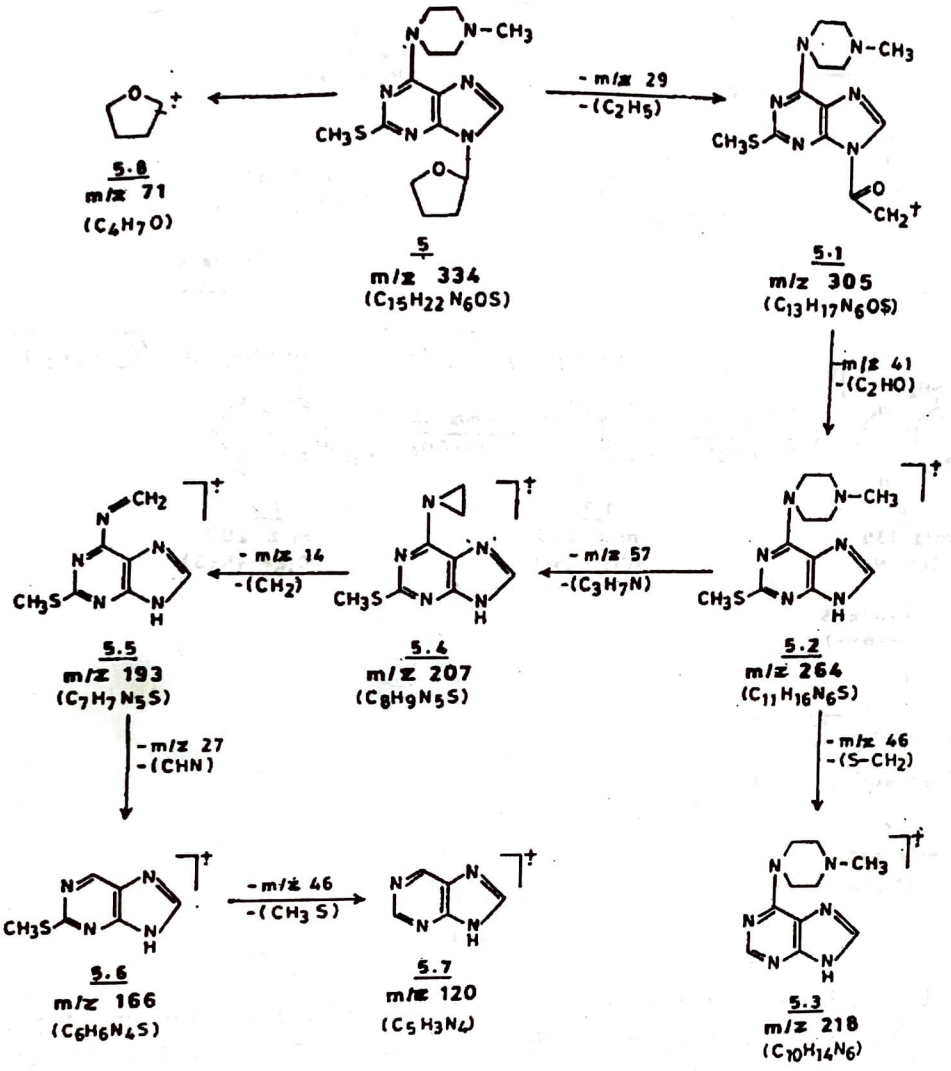
Scheme 1

amino group to give base peak at *m/z* 120, the purine ring system. Compounds **5-8** exhibited a rearrangement in the amino group followed by the removal of the amino and then loss of methylthio group. Apart from this a peak at *m/z* 71 had been observed in all the compounds which is assigned to tetrahydrofuran moiety.

Results and Discussion

Mass fragmentation pattern of 6-(*p*-ethyltoluylamino)-2-methylthio-9-tetrahydrofuranylpurine (**1**) is described in Scheme 1. Compound **1** gives the major peaks at *m/z* 369 (M^+), 340, 299, 253, 135, 120, 71. The peaks at *m/z* 340 represent fragmentation in tetrahydrofuran moiety attached at position-9 of purine base by the rearrangement in bonds between 2′, 3′ and 4′ and oxygen to provide radical ion (**1.1**) followed by the loss of rearranged moiety confirmed by the peak at *m/z* 299 (**1.2**). The next peak at *m/z* 253 was obtained by the fragmentation of methylthio group at position-2 (**1.3**) peak at *m/z* 135 (**1.4**) which indicates the loss of ethyltoluyl group (**1.3**) resulting in adenine radical ion. In the same sequence this radical ion losses 15 units to give the base peak at *m/z* 120 assigned to purine nucleus[3] (**1.5**). Another peak at *m/z* 71 (**1.6**) was assigned to tetrahydrofuran radical ion.

Similarly, mass fragmentation pattern of 6-(*N*-methylpiperazanyl)-2-methylthio-9-tetrahydrofuranylpurine (**5**) is described in Scheme 2. Compound **5** gives the major peaks at *m/z* 334 (M^+), 305, 264, 218, 207, 193, 166, 120, 71. The tetrahydrofuranyl group had been observed to be fragmented in the same manner as for **1** giving the peak at *m/z* 264 (**5.2**). The next fragmentation was observed when methylthio group was cleaved to furnish the peak at *m/z* 218 (**5.3**), the variation in the fragmentation mode was observed in compounds **1-4** and **5-8** in the step where (**5.2**) undergoes fragmentation when piperazanyl group rearranged to give ethylamino group and finally cyclized[4] to give **5.4** at *m/z* 207. (**5.4**) on further fragmentation gave an imino radical ion (**5.5**) at *m/z* 193 followed by the loss of imino group at *m/z* 166 (**5.6**). The latter further by the loss of 46 units, i.e. methylthio group provided purine base at *m/z* 120 which was observed as most abundant peak. The peak at *m/z* 71 (**5.8**) indicates tetrahydrofuran moiety like in Scheme 1.



Scheme 2

Experimental

The mass spectra of these compound were run on a JEOL JMS D-300 spectrometer using the direct inject system.

Acknowledgement

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