Method I. $SOCl_2$ (100 ml, 166 g, 1.40 moles) was added to 24.8 g (0.20 mole) of 2-pyrazinecarboxylic acid (Aldrich Organic Chemicals) suspended in 150 ml of dry C_6H_6, and the reaction mixt was refluxed 90 min. The solvent and excess $SOCl_2$ were removed *in vacuo* yielding a dark red residue which decompd readily on standing. To the freshly prepared 2-pyrazinoyl chloride was added 0.48 mole of the appropriate arom amine dissolved in 300 ml of dry C_6H_6. After being refluxed for 5 hr, the hot reaction mixt was filtered, and the filtrate was concd to 200 ml. Addn of 400 ml of petr ether and cooling gave solid 2-pyrazinecarboxanilide. Recrystn was achieved in aqueous MeOH (3:1) (charcoal) and repeated.

Method II. A mixt of 49.6 g (0.40 mole) of 2-pyrazinecarboxylic acid, 20 ml (30.4 g, 0.24 mole) of PCl_3, and 0.84 mole of the arom amine in 1000 ml of dry C_6H_6 was refluxed 5 hr. The hot reaction mixt was filtered, and the filtrate was evapd to dryness. The crude 2-pyrazinecarboxanilide was recrystd as above. All the anilides were soluble in 6 *M* HCl but insoluble in 3 *M* HCl, and they were greater than 2% soluble in propylene glycol at room temp.

2-Pyrazinecarboxanilide. A yield of 57.2 g (72%) of beige crystals was obtained: mp 123–125°; ν_{max}^{KBr} 3400, 1675, 1600, 1535, 1470, 755 cm^{-1}. *Anal.* ($C_{11}H_9N_3O$) C, H, N.

2-Pyrazinecarbox-2′-toluidide. A yield of 74.0 g (87%) of beige crystals was obtained: mp 113–114°; ν_{max}^{KBr} 3400, 1680, 1580, 1535, 1460, 750 cm^{-1}. *Anal.* ($C_{12}H_{11}N_3O$) C, H, N.

2-Pyrazinecarbox-2′,6′-ylidide. A yield of 69.6 g (77%) of beige crystals was obtained: mp 110–112°; ν_{max}^{KBr} 3400, 1680, 1525, 1470, 1400, 765 cm^{-1}. *Anal.* ($C_{13}H_{13}N_3O$) C, H, N.

2-Pyrazinecarbox-2′,4′,6′-mesidide. A yield of 79.0 g (82%) of beige crystals was obtained: mp 124–125°; ν_{max}^{KBr} 3400, 1680, 1525, 1400, 840 cm^{-1}. *Anal.* ($C_{14}H_{15}N_3O$) C, H, N.

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2,5-Anhydro-1-deoxy-1-[(6-methylthio)purin-9-yl]-D-allitol†

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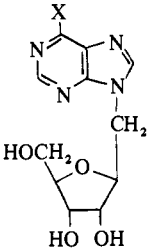
The reasons for our interest in the purin-9-yl-D-allitols and the preparation of 2,5-anhydro-1-(6-chloropurin-9-yl)-1-deoxy-3,4-*O*-isopropylidene-D-allitol (**1**) have been outlined.[1] Compound **1**, prepared by the method described in the Experimental Section, was converted to 2,5-anhydro-1-deoxy-1-(6-mercaptopurin-9-yl)-D-allitol (**2**), which was methylated to give 2,5-anhydro-1-deoxy-1-[(6-methylthio)-purin-9-yl]-D-allitol (**3**), a homolog of the potent anticancer agent 6-(methylthio)purine ribonucleoside.[2]

These purin-9-yl allitols (**2** and **3**) and 1-adenin-9-yl-2,5-anhydro-1-deoxy-D-allitol were evaluated for their toxicity



2, X = SH
3, X = SCH_3

to human epidermoid carcinoma cells No. 2 in culture,[3] but they did not significantly inhibit the growth of these cells at 100 μg/ml, the highest level tested.

Experimental Section‡

2,5-Anhydro-1-deoxy-1-(6-mercaptopurin-9-yl)-D-allitol (2). Anhydro-1-deoxy-1-(5-amino-6-chloropyrimidin-4-yl)amino-3,4-*O*-2,5-isopropylidene-D-allitol (1 g, 3 mmoles) in ethyl orthoformate (8 ml) contg 0.35 ml of concd HCl was allowed to stand overnight (tlc, 9:1 $CHCl_3$–MeOH) before the addn of thiourea (304 mg, 4 mmoles) in alcohol (12 ml). This soln was then heated at 70–80° for 2 hr, cooled, and filtered. A soln of the ppt in 0.1 *N* NaOH was filtered and acidified with glacial HOAc. The ppt [tlc, 9:1 $CHCl_3$–MeOH, mp 260–264°] was collected by filtration and suspended in 65% EtOH contg 6.7 ml of 0.6 *N* HCl, and the suspension was heated at 100° for 30 min. The soln was filtered before neutralization with 1 *N* NaOH and concd *in vacuo*. The solids obtained were recrystd from H_2O: yield 290 mg; tlc, 9:1 $CHCl_3$–MeOH; mp 248–250°; $[\alpha]^{24}D$ −38.5° ±1.6° (*c* 0.92, 0.1 *N* NaOH); λ_{max} in nm (pH 1) 226 (8.85), 324 (22.4); (pH 7) 227 (9.76), 320 (25.2); (pH 13) 233 (113.9), 310 (23.2). *Anal.* ($C_{11}H_{14}N_4O_4S$) C, H, N.

2,5-Anhydro-1-deoxy-1-[(6-methylthio)purin-9-yl]-D-allitol (3). To a soln of 2,5-anhydro-1-deoxy-1-(6-mercaptopurin-9-yl)-D-allitol (175 mg, 0.58 mmole) in H_2O contg 1 equiv of NaOH was added dropwise MeI (0.29 ml) with vigorous stirring, and the mixt was stirred for 3 hr before it was evapd to dryness. The residue, dissolved in EtOH (20 ml), was treated with Amberlite MB1 resin suspended in H_2O (20 ml). The resin was removed by filtration and the filtrate evapd to dryness. The residue was recrystd twice from EtOH: yield 100 mg (92%); tlc, 1:1 $CHCl_3$–EtOAc, 9:1 PhH–MeOH; 1:1 PhH–Et_2O; mp 115°, $[\alpha]^{25.5}D$ −41.3° ± 0.6° (*c* 1.06, EtOH); λ_{max} in nm (pH 1) 287 (sh), 294 (17.7); (pH 7, 13) 286 (19.7), 292 (19.5). *Anal.* ($C_{12}H_{16}N_4O_4S \cdot 0.5EtOH$) C, H, N. The presence of EtOH in the sample was confirmed by mass spectrometry, *m/e* 312 (calcd 312).

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‡Silica gel H (Brinkmann) was used for thin-layer analyses (tlc). Chromatographic homogeneity was established for all reported compds in the solvents indicated. The uv spectra were detd with a Cary Model 14 spectrophotometer, the mass spectrum with a Hitachi Perkin-Elmer RMU-7, and the optical rotations with a Rudolph Model 80 polarimeter. Melting points were detd with a Mel-Temp apparatus.