ON 6-C-SUBSTITUTED PURINE AND 9-β-D-RIBOFURANOSYLPURINE DERIVATIVES: SYNTHESIS OF 6-DICYANOMETHYLPURINES AND 3-AMINO-2-(PURIN-6-YL)ACRYLONITRILES

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6-Dicyanomethyl-9-(2,3,5-tri-O-benzoyl-β-D-ribofuranosyl)purine (1a), 6-dicyanomethyl-9-β-D-ribofuranosylpurine (1b), 6-dicyanomethyl-9-methoxymethyl-9H-purine (1c), and 6-dicyanomethylpurine (1d) were synthesized in good yields from the corresponding 6-chloropurines with malononitrile and sodium hydride in dimethyl sulfoxide(DMSO). Hydrogenation of 1a,c,d over palladium as a catalyst afforded the corresponding 3-amino-2-(purin-6-yl)acrylonitriles [2a,c,d (R^1=R^2=H)]. On reaction with primary and secondary amines such as methylamine, ethanolamine, benzylamine, aniline, dimethylamine, pyrrolidine, and morpholine , 2a,c,d furnished N-substituted 3-amino-2-(purin-6-yl)acrylonitriles [3a-d (R^1≠ H, R^2= H), 4a-d(R^1≠H, R^2≠ H)].

The configurations of the aminoacrylonitriles were detected by means of nuclear magnetic resonance spectroscopy: N,N-Disubstituted aminoacrylonitriles (4a-d) exist as Z-form exclusively, while 2a-d and N-monosubstituted aminoacrylonitriles (3a-d) exist as an equilibrated mixture of E- and Z-form, the latter being the major configuration in DMSO-d_6.