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

Tadashi Miyazaki, Nosimitsu Hasegawa, and Hiroshi Sugawara
School of Pharmaceutical Sciences, Showa University
Hatanodai, Shinagawa-ku, Tokyo, 142 Japan

6-Dicyanomethyl-9-(2,3,5-tri-O-benzoyl-D-D-ribofuranosyl)purine (1a), 6-dicyanomethyl-9-D-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=r=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'=H), 4a-d (R'=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-monomosubstituted aminoacrylonitriles (3a-d) exist as an equilibrated mixture of E- and Z-form, the latter being the major configuration in DMSO-d6.

\[ \text{N}=\text{C} \quad \text{CN} \]

\[ \text{H} \quad \text{N} \quad \text{C} \quad \text{CN} \]

\[ \text{R} \]

\[ \text{N} \quad \text{C} \quad \text{CN} \]

\[ \text{H} \quad \text{N} \quad \text{C} \quad \text{CN} \]

\[ \text{R} \]

\[ \text{E} \]

\[ \text{Z} \]

\[ \text{R}^1 \quad \text{N} \quad \text{R}^2 \]

\[ \text{H} \quad \text{C} \quad \text{N} \]

\[ \text{R} \]

\[ \alpha: R= \]

\[ \beta: R= \]

\[ \gamma: R= \]

\[ \delta: R= \]

-118-