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Non-natural nucleosides bearing 4-aryldiazenylpyrazole aglycone

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Experimental

3,5-Dimethyl-4-[(4-methylphenyl)diazenyl]-1*H*-pyrazole (1a). Yield 92%, mp 145−146 ºC (lit.[1], mp 157 ºC).

3-Methyl-4-[(4-methylphenyl)diazenyl]-5-nonafluorobutyl-1*H*-pyrazole (1b). Yield 89%, mp 118−120 ºC. IR (FTIR), ν, cm^{-1}: 3183 (N–H), 1134-1264 (C-F). ^{1}H NMR ($CDCl_3$), δ (*J*, Hz): 2.42 (3H, s, $C_6H_4C\underline{H}_3$); 2.63 (3H, s, 3-CH_3); 7.28–7.30 (2H, m, H_m, C_6H_4); 7.72–7.74 (2H, m, H_o, C_6H_4). ^{19}F NMR, *δ* (*J*, Hz): 35.9-36.0 (2F, m, CF_2); 39.2-39.3 (2F, m, CF_2); 52.9-53.0 (2F, m, CF_2); 80.8-80.9 (3F, m, CF_3). Found, %: C 43.24; H 2.45; N 13.54. $C_{15}H_{11}N_4F_9$. Calculated, %: C 43.07; H 2.65; N 13.40.

1-(2,3,5-Tri-*O*-acetyl-*β*-D-ribofuranosyl)-3-nonafluorobutyl-5-methyl-4-[(4-methylphenyl)diazenyl]-1*H*-pyrazole (2b). Orange oil, $[\alpha]_D$ -25.22 (c 1.013, MeOH). IR (FTIR), ν, cm^{-1}: 1751 (C=O), 1212-1233 (C-F). ^{1}H NMR ($CDCl_3$), δ (*J*, Hz): 2.05 (3H, s, CH_3CO_2); 2.14 (6H, s, CH_3CO_2); 2.43 (3H, s, $C_6H_4C\underline{H}_3$); 2.68 (3H, s, 5-CH_3); 4.15 (1H, dd, $^{5',5''}J$ = 12.7, $^{4',5'}J$ = 5.6, H5'); 4.41-4.46 (2H, m, H5'' and H4'); 5.72 (1H, t, $^{3',2'}J$ = 5.2, H3'); 5.95 (1H, dd, $^{3',2'}J$ = 5.2, $^{1',2'}J$ = 3.1, H2'); 5.99 (1H, d, $^{1',2'}J$ = 3.1, H1'), 7.28–7.30 (2H, m, H_m, C_6H_4); 7.71–7.74 (2H, m, H_o, C_6H_4). ^{19}F NMR, *δ* (*J*, Hz): 36.1-36.2 (2F, m, CF_2); 39.5-39.6 (2F, m, CF_2); 53.3 (2F, td, *J* = 41.6, 12.2, CF_2); 80.8-80.9 (3F, m, CF_3). Mass spectrum, *m/z* (I_{rel}(%): 676 $[M]^+$ (7), 418 $[M - C_{11}H_{14}O_7]^+$ (12), 327 $[M - C_{11}H_{14}O_7 - C_6H_4CH_3]^+$ (6), 259 $[C_{11}H_{14}O_7]^+$ (8), 123 $[C_6H_7N_4]^+$ (44), 95 $[C_6H_7N_2]^+$ (7), 91 $[C_7H_7]^+$ (18), 43 $[CH_3CO]^+$ (100). Found, %: C 46.28; H 3.68; N 8.42. $C_{26}H_{25}N_4F_9O_7$. Calculated, %: C 46.16; H 3.73; N 8.28.

1-(2,3,5-Tri-*O*-acetyl-*α*-D-ribofuranosyl)-3-nonafluorobutyl-5-methyl-4-[(4-methylphenyl)diazenyl]-1*H*-pyrazole (3b). Orange oil, $[\alpha]_D$ 31.08 (c 1.05, CH_2Cl_2). ^{1}H NMR ($CDCl_3$), δ (*J*, Hz): 1.82 (3H, s, CH_3CO_2); 2.10 (3H, s, CH_3CO_2); 2.14 (3H, s, CH_3CO_2); 2.43

(3H, s, $C_6H_4C\underline{H}_3$); 2.62 (3H, s, 5-CH_3); 4.28 (1H, dd, $^{5',5''}J$ = 12.4, $^{4',5'}J$ = 4.2, H5'); 4.47 (1H, dd, $^{5',5''}J$ = 12.4, $^{4',5''}J$ = 2.6, H5''); 5.04 (1H, m, H4'); 5.32 (1H, dd, $^{4',3'}J$ = 7.5, $^{3',2'}J$ = 6.6, H3'); 5.47 (1H, dd, $^{3',2'}J$ = 6.6, $^{1',2'}J$ = 6.1, H2'); 6.36 (1H, d, $^{1',2'}J$ = 6.1, H1'), 7.28–7.30 (2H, m, H_m, C_6H_4); 7.71–7.74 (2H, m, H_o, C_6H_4). ^{19}F NMR, δ (*J*, Hz): 36.1-36.2 (2F, m, CF_2); 39.7-39.8 (2F, m, CF_2); 53.4-53.5 (2F, m, CF_2); 80.8-80.9 (3F, m, CF_3). Mass spectrum, *m/z* (I_{rel}(%): 676 $[M]^+$ (3), 418 $[M - C_{11}H_{14}O_7]^+$ (9), 327 $[M - C_{11}H_{14}O_7 - C_6H_4CH_3]^+$ (9), 259 $[C_{11}H_{14}O_7]^+$ (13), 91 $[C_7H_7]^+$ (36), 43 $[CH_3CO]^+$ (100).

1-(*β*-D-Ribofuranosyl)-3-nonafluorobutyl-5-methyl-4-[(4-methylphenyl)-diazenyl]-1*H*-pyrazole (4b). Yield 82%, yellow powder, mp 171−173 ºC, $[\alpha]_D$ -11.50 (c 1.067, CH_3OH). IR (FTIR), ν, cm^{-1}: 3349 (O–H), 1225 (C-F). ^{1}H NMR (CD_3CN), δ (*J*, Hz): 2.41 (3H, s, $C_6H_4C\underline{H}_3$); 2.68 (3H, s, 5-CH_3); 3.55-3.58 (1H, m, H5'); 3.70-3.75 (1H, m, H5''); 4.29 (1H, dd, $^{4',5'}J$ = 7.9, $^{4',5''}J$ = 4.3, H4'); 4.40-4.42 (1H, m, H3'); 4.65 (1H, m, H2'); 5.92 (1H, d, $^{1',2'}J$ = 3.4, H1'); 7.34–7.36 (2H, m, H_m, $C_6\underline{H}_4CH_3$); 7.70–7.72 (2H, m, H_o, $C_6\underline{H}_4CH_3$). ^{19}F NMR (CD_3CN), δ (*J*, Hz): 36.2-36.4 (2F, m, CF_2); 41.7-41.8 (2F, m, CF_2); 55.9-56.0 (2F, m, CF_2); 82.7 (3F, tt, *J* = 9.9, 2.8, CF_3). Found, %: C 43.37; H .3.62; N 10.25. $C_{20}H_{19}N_4F_9O_4$. Calculated, %: C 43.65; H 3.48; N 10.18.

References

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