1H,7H-Pyrano[3,2-e]-v-benzotriazol-7-one. A New Ring System

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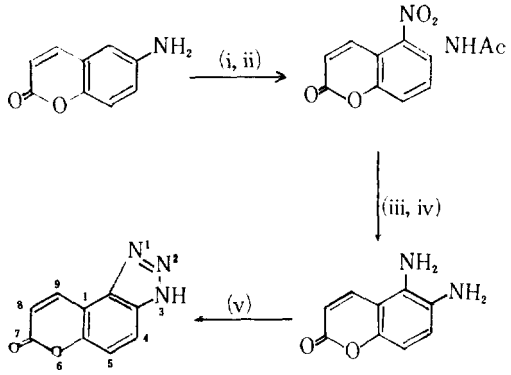
Heterocyclic ring systems arising from the condensation of a coumarin ring to other heterocyclic rings have been reported in the literature. Some of these contain a pyrrole or a pyridine ring fused to the benzene ring of the coumarin molecule[1] while in some others heterocyclic rings are fused to the pyran ring of the coumarin system.[2-4] Benzopyrans containing a fused five membered system have been also found to possess pharmacological properties. Angalecin a furobenzopyran has spasmolytic activity[5] while another benzopyran containing a v-triazole ring is also of interest as a potential antiasthmatic agent.[6] In the present communication we would like to report the synthesis of a new ring system-1H,7H-pyrano[3,2-e]-v-benzotriazol-7-one (I) in which a v-triazole ring has been fused to the benzene ring of coumarin.

The synthesis of the ring system is presented in Scheme 1. 6-Aminocoumarin (II)[7], after acylation,[8] was nitrated with mixed acids (H_2SO_4-HNO_3) at 0°C-5°C for 24 h to afford



(i) Ac_2O/NaOAc; ii HNO_3/H_2SO_4; iii H_3O^+
(iv) Fe/HCl; $NaNO_2$/AcOH

6-acetylamino-5-nitrocoumarin (III) in 70% yield.[9] The substitution of the nitro group has been occurred at the 5 position of the coumarin ring, which is borne out by the ^{1}HNMR spectrum of III, displaying four doublets due to the protons at 3, 4, 7 and 8 position of III. Hydrolysis of III in refluxing 10% aqueous H_2SO_4 for 2 h in 80% yield[10] followed by the reduction with iron powder and hydrochloric acid gave the key intermediate 5,6-diaminocoumarin (IV) in 53% yield,[11] which on diazotization with sodium nitrite in aqueous acetic acid at room temperature furnished 1H,7H-pyrano[3,2-e]-v-benzotriazol-7-one (1).[12] The new heterocyclic compound (I) was thoroughly characterized through its elemental analysis, IR, and ^{1}HNMR spectra.

Further work on this and related systems is in progress.

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9. m.p. 215-216°C; ^{1}HNMR (CF_3COOH) δ 2.49 (*s*, 3H, CH_3), 6.90 (*d*, J = 10 Hz, 1H, H-3), 7.78 (*d*, J = 9 Hz, 1H, H-8), 8.25 (*d*, J = 10 Hz, 1H, H-4), 8.26 (*d*, J = 9 Hz, 1H, H-7), 9.15 (*s*, 1H, NH); IR(KBr) 3100-3000, 1752, 1748, 1525, 1355cm^{-1}. Anal. Calcd for $C_{11}H_8N_2O_5$: C, 53.23; H, 3.25; N, 11.29. Found: C, 52.98; H, 3.21; N, 11.09.
10. m.p. 225-227 °C; IR(KBr) 3450, 3320, 1520, 1380 cm^{-1}. Anal. Calcd for $C_9H_6N_2O_4$: C, 52.43; H, 2.93; N, 13.59. Found: C, 52.34; H, 2.88; N, 13.30.
11. m.p. 195-196 °C; ^{1}HNMR(DMSO-d_6) δ 6.18 (*d*, J = 10 Hz, 1H, H-3), 6.39 (*d*, J = 8 Hz, 1H, H-8), 6.82 (*d*, J = 8 Hz, 1H, H-7), 8.25 (*d* J = 10 Hz, 1H, H-4), 5.00 (*m*, 4H, NH_2) IR(KBr) 3450-3200, 1700 cm^{-1}. Anal. Calcd for $C_9H_8N_2O_2$: C, 61.36; H, 4.58; N. 15.90. Found; C, 61.23; H, 4.36; N, 15.70.
12. m.p. 259-260 °C; ^{1}HNMR(DMSO-d_6) δ 6.60 (*d*, J = 10 Hz, 1H, H-8), 7.36 (*d*, J = 10 Hz, 1H, H-5), 8.04 (*d*, J = 10 Hz, 1H, H-4), 8.34 (*d* J = 10 Hz, 1H, H-9); IR(KBr) 3450, 1760 cm^{-1}. Anal. Calcd for $C_9H_5N_3O_2$: C, 57.76; H, 2.69; N, 22.45. Found: C, 58.00; H, 2.89; N, 22.34.