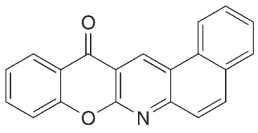
A Facile One-Pot Synthesis of Functionalized 1,5-Dihydro-2*H*-[1]benzopyrano[2,3-*b*]pyridin-5-ones

by **Abbas Ali Esmaeili*** and **Omid Ghareghani**

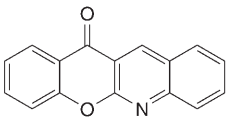
Department of Chemistry, University of Birjand, P. O. Box 97175/615, Birjand, Iran
(fax: (0098561)2230009; e-mail: aa_esmaeili@yahoo.com)

The highly reactive 1:1 intermediate generated in the reaction between dialkyl acetylenedicarboxylate (= but-2-ynedioic acid dialkyl ester) **4** and triphenylphosphine was trapped by 2-amino-4-oxo-4*H*-1-benzopyran-3-carboxaldehydes **5** to yield highly functionalized dialkyl-1,5-dihydro-5-oxo-1-phenyl-2*H*-[1]benzopyrano[2,3-*b*]pyridine-2,3-dicarboxylates in high yield.

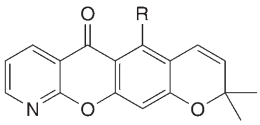
1. Introduction. – The 4*H*-chromen-4-one (=4*H*-1-benzopyran-4-one) moiety is an integral part of many natural products [1–4]. Derivatives of 4*H*-chromen-4-one have also drawn much attention due to their activity against the human-immunodeficiency virus (HIV-1) [5][6] that causes the acquired immune deficiency syndrome (AIDS), and to broad pharmacological activities [7–9]. In addition, the chromenone moiety forms the important component of pharmacophores of a number of biologically active molecules of synthetic as well as natural origin, and many of them have useful medicinal applications [10–12]. Consequently, chromenone chemistry continues to draw considerable interest of synthetic organic and medicinal chemists [12–20]. For example hetero-annulated chromenones **1** and **2** have pharmacological activities [21]. Furthermore, 'azapyranoxanthenon' (=2*H*,6*H*-pyrano[3′,2′:6,7][1]benzopyrano[2,3-*b*]pyridin-6-one) derivatives **3** were reported to have cytotoxic activity against the murine L1210 leukemia and the human solid tumor HT-29 lines [22].



1



2



3

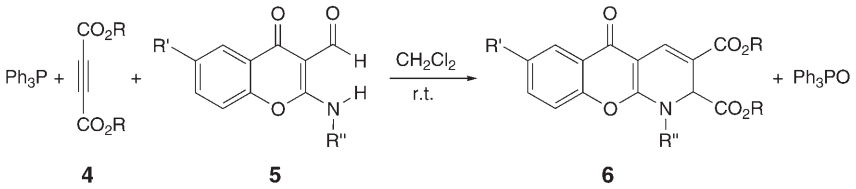
Because of their pharmacological importance, the synthesis of heterocycles fused with a chromenone moiety has attracted much attention [23–25], and 4-oxo-4*H*-1-benzopyran-3-carboxaldehyde has emerged as a valuable synthon for the incorporation of the chromenone moiety into a number of molecular frameworks [26–29]. The 2-(alkylamino)- or 2-(arylamino)-4-oxo-4*H*-1-benzopyran-3-carboxaldehydes have been utilized recently in the synthesis of several heterocycles [21][30–33].

Over the years, the *Wittig* reaction has evolved to include many variations that constitute some of the most powerful processes for the construction of C=C bonds

[34]. The importance of intramolecular *Wittig* reactions [35] in the synthesis of cycloalkenes and unsaturated heterocyclic compounds can hardly be overestimated. Our one-pot synthesis of highly functionalized 1,5-dihydro-5-oxo-2*H*-[1]benzopyrano[2,3-*b*]pyridine-2,3-dicarboxylates **6** comprised such a *Wittig* reaction.

2. Results and Discussion. – In this study, we wish to describe a further use of 2-(alkylamino)- and 2-(arylamino)-4-oxo-4*H*-1-benzopyran-3-carboxaldehydes **5** in reactions with a number of acetylenic esters **4** in the presence of Ph_3P in dry CH_2Cl_2 at room temperature (*Scheme 1*). The highly functionalized products, *i.e.*, dialkyl 1-aryl- and 1-alkyl-1,5-dihydro-5-oxo-2*H*-[1]benzopyrano[2,3-*b*]pyridine-2,3-dicarboxylates **6**, were obtained in 92–97% yield within 20–60 min (*Table*). ^{1}H- and ^{13}C-NMR spectra of the crude products clearly indicated the formation of derivatives **6**. Products other than **6** could not be detected. Structures **6a**–**h** were assigned on the basis of the elemental analyses and IR, ^{1}H- and ^{13}C-NMR, and MS data of the isolated products.

Scheme 1[a])



4 **5** **6**

[a]) For R, R′, and R″, see *Table*.

Table. *Products* **6** *of the Reaction of 2-(Alkylamino)- and 2-(Arylamino)-4-oxo-4*H*-1-benzopyran-3-carboxaldehydes* **5** *with Dialkyl Acetylenedicarboxylates* **4** *in the Presence of Ph_3P*

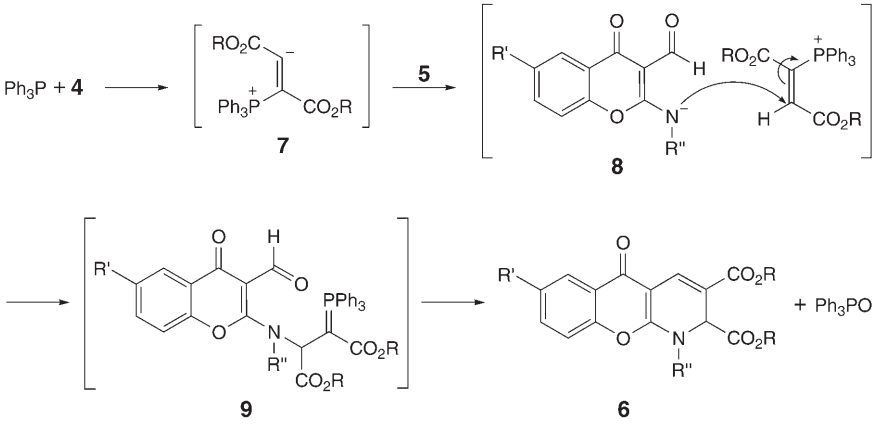
	R	R′	R″	Time [min]	Yield [%][a])
6a	Me	H	Ph	25	97
6b	Me	H	CH_2CO_2Et	20	93
6c	Me	H	2-$MeOC_6H_4$	30	96
6d	Me	Cl	Ph	30	96
6e	Et	H	Ph	45	96
6f	Et	H	CH_2CO_2Et	40	92
6g	Et	H	2-$MeOC_6H_4$	60	95
6h	Et	Cl	Ph	60	95

[a]) Isolated material.

The ^{1}H-NMR spectrum of **6a** exhibited two single sharp lines for the MeO groups at δ 3.71 and 3.82, a sharp *s* for the methine proton at δ 5.65, and a single sharp line for the olefinic proton at δ 8.06, along with characteristic *m* with appropriate chemical shifts and coupling constants for the aromatic protons. The ^{1}H- decoupled ^{13}C-NMR spectrum of **6a** showed 20 distinct resonances in agreement with the structure of the product. The ^{1}H- and ^{13}C-NMR spectra of **6b**–**h** were similar to those of **6a**, except for the signals of the substituent at N(1) and the ester moieties, which exhibited characteristic resonances with appropriate chemical shifts and coupling constants (see *Exper. Part*).

A plausible reaction mechanism for the transformation **4** + **5** → **6** in the presence of Ph_3P is proposed in *Scheme 2*. It is conceivable that the initial event is the formation of a 1,3-dipolar intermediate **7** from Ph_3P and the acetylenic compound **4** [36–39], which is subsequently protonated by the 2-amino-3-carboxaldehyde **5** to give the ion pair **8**. Nucleophilic attack of the N-atom of the conjugate base of the NH acid **8** at the alkenylphosphonium cation then produces ylide **9**, which is converted to **6** by an intramolecular *Wittig* reaction.

Scheme 2



In conclusion, the present method has the advantage that not only neutral conditions can be applied to the transformation but also the starting materials can be mixed without any activation or modification. The simplicity of the procedure makes it an interesting alternative to multistep approaches to chromenone derivatives fused to a heterocycle. Thus, the described reaction provides an efficient one-pot method for the preparation of highly functionalized dialkyl 1-aryl- and 1-alkyl-1,5-dihydro-5-oxo-2*H*-[1]benzopyrano[2,3-*b*]pyridine-2,3-dicarboxylates of potential synthetic and pharmaceutical interest.

Experimental Part

General. M.p.: *Electrothermal 9100* apparatus; uncorrected. IR Spectra: *Perkin-Elmer 783* IR spectrophotometer; in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker DRX-250-Avance* spectrometer at 500 (^1H) and 125.7 MHz (^{13}C); $CDCl_3$ solns.; δ in ppm, J in Hz. MS: *Shimadzu GCMS-QP5050* mass spectrometer, ionization potential 70 eV; in *m*/*z* (rel.%) Elemental analyses: *Heraeus CHN-O-Rapid* analyzer.

*Dimethyl 1-Aryl- and 1-Alkyl-1,5-dihydro-5-oxo-2*H*-[1]benzopyrano[2,3-*b*]pyridine-2,3-dicarboxylates* **6**: *General Procedure.* To a magnetically stirred soln. of a 4-oxo-2-amino-4*H*-1-benzopyran-3-carboxaldehyde **5** [21] (2 mmol) and Ph_3P (2 mmol) in CH_2Cl_2 (3 ml), but-2-ynedioic acid dimethyl ester (**4**; R = Me) (2 mmol) was added dropwise at −5° within 10 min. The mixture was then allowed to warm up to r.t. and stirred for 15 min. The solvent was evaporated and the residue crystallized from EtOH: **6**.

*Dimethyl 1,5-Dihydro-5-oxo-1-phenyl-2*H-*[1]benzopyrano[2,3-*b*]pyridine-2,3-dicarboxylate* (**6a**). Yield 0.38 g (97%). M.p. 204–205°. IR (KBr): 3070 (arom. C–H), 2950 (aliph. C–H), 1745, 1700 (2 CO_2Me), 1625 (CO), 1215 (C–O). ^{1}H-NMR: 3.71 (*s*, Me); 3.80 (*s*, Me); 5.65 (*s*, CHN); 7.09 (*d*, $^3J = 8.3$, 1 arom. H); 7.33 (*t*, $^3J = 7.41$, 1 arom. H); 7.38–7.51 (*m*, 6 arom. H); 8.06 (*s*, 1 olef. H); 8.18 (*d*, $^3J = 7.66$, 1 arom. H). ^{13}C-NMR: 51.98 (Me); 52.98 (Me); 62.60 (CHN); 98.84 (C(4a)); 110.94 (C(3)); 116.99 (C(9)); 122.56 (C(5a)); 125.45 (C(6)); 126.24 (C(7)); 126.53; 128.22; 129.53 (arom. CH); 131.53 (C(4)); 132.52 (C(8)); 139.89 (arom. C); 153.35 (C(9a)); 159.74 (C(10a)); 165.13, 169.87 (2 *C*O_2Me); 172.91 (C(5)). EI-MS: 391 (1, M^+), 360 (2, $[M - MeO]^+$), 333 (20), 332 (100, $[M - CO_2Me]^+$), 273 (3), 272 (4), 196 (4), 77 (18, $C_6H_5^+$), 59 (6, CO_2Me^+). Anal. calc. for $C_{22}H_{17}NO_6$ (391.38): C 67.52, H 4.38, N 3.58; found: C 68.0, H 4.4, N 3.6.

*Dimethyl 1-(2-Ethoxy-2-oxoethyl)-1,5-dihydro-5-oxo-2*H-*[1]benzopyrano[2,3-*b*]pyridine-2,3-dicarboxylate* (**6b**). Yield 0.371 g (93%). M.p. 206–208°. IR (KBr): 3090 (arom. C–H), 2974, 2924 (aliph. C–H), 1750, 1675 (2 CO_2Me), 1650 (CO), 1500 (arom. C=C). ^{1}H-NMR: 1.21 (*t*, $^3J = 5.7$, Me); 3.65 (*s*, MeO); 3.74 (*s*, MeO); 4.21 (*q*, $^3J = 7.13$, CH_2O); 4.34 (*s*, CH_2N); 5.33 (*s*, CHN); 7.59 (*t*, $^3J = 7.5$, 1 arom. H); 7.33–7.45 (*m*, 2 arom. H); 7.96 (*s*, 1 olef. H); 8.1 (*d*, $^3J = 7.1$, 1 arom. H). ^{13}C-NMR: 14.02 (Me); 49.57 (CH_2N); 51.82 (MeO); 52.86 (MeO); 61.29 (CH_2O); 61.97 (CHN); 96.96 (C(4a)); 110.70 (C(3)); 116.56 (C(9)); 122.40 (C(5a)); 125.60 (C(6)); 126.26 (C(7)); 131.56 (C(8)); 132.78 (C(4)); 153.03 (C(9a)); 160.38 (C(10a)); 165.17, 169.15, 167.31 (3 CO, ester); 172.09 (C(5)). EI-MS: 401 (1, M^+), 402 (1, $[M + 1]$), 370 (1, $[M - MeO]^+$), 343 (21), 342 (100, $[M - CO_2Me]^+$), 328 (2), 315 (11), 314 (61), 300 (1, $[M - NCH_2CO_2Et]^+$), 196 (5, $[M - 2\ CO_2Me - CH_2CO_2Et]^+$), 59 (6, CO_2Me^+). Anal. calc. for $C_{20}H_{19}NO_8$ (401.38): C 59.85, H 4.77, N 3.49; found: C 60.0, H 4.8, N 3.5.

*Dimethyl 1,5-Dihydro-1-(2-methoxyphenyl)-5-oxo-2*H-*[1]benzopyrano[2,3-*b*]pyridine-2,3-dicarboxylate* (**6c**). Yield 0.405 g (96%). M.p. 210–212°. IR (KBr): 3000 (arom. C–H), 2920 (aliph. C–H), 1745 and 1700 (2 CO_2Me), 1625 (CO), 1500 (arom. C=C), 1212 (C–O). ^{1}H-NMR: 3.67, 3.73, 3.79 (3*s*, 3 MeO); 5.54 (*s*, CHN); 6.97–7.04 (*m*, 3 arom. H); 7.22–7.49 (*m*, 3 arom. H); 7.55 (*d*, $^3J = 6.0$, 1 arom. H); 8.07 (*s*, 1 olef. H); 8.16 (*s*, 1 arom. H). ^{13}C-NMR: 51.81, 52.71, 55.81 (3 MeO); 62.22 (CHN); 98.09 (C(4a)); 110.86 (C(3)); 112.02 (arom. CH); 116.82 (arom. CH); 120.85 (arom. CH); 122.58 (C(5a)); 125.22 (C(6)); 126.15 (C(7)); 127.98 (arom. CH); 129.49 (arom. C); 129.79 (arom. CH); 131.6 (C(8)); 132.61(C(4)); 153.3 (C(9a)); 154 (arom. C); 160.29 (C(10a)); 170.06, 165.24 (2 CO_2Me); 172.76 (C(5)). EI-MS: 362 (100, $[M - CO_2Me]^+$), 363 (24, $[M + 1 - CO_2Me]^+$), 318 (28, $[M - C_7H_4O]^+$), 304 (2), 288 (2.5), 196 (4, $[M - 2\ CO_2Me - MeOC_6H_4]^+$), 77 (26, $C_6H_5^+$), 59 (9, CO_2Me^+). Anal. calc. for $C_{23}H_{19}NO_7$ (421.41): C 65.56, H 4.54, N 3.32; found: C 64.0, H 4.4, N 3.2.

*Dimethyl 7-Chloro-1,5-dihydro-5-oxo-1-phenyl-2*H-*[1]benzopyrano[2,3-*b*]pyridine-2,3-dicarboxylate* (**6d**). Yield 0.411 g (96%). M.p. 210–212°. IR (KBr): 3050 (arom. C–H), 2950 (aliph. C–H), 1745 and 1700 (2 CO_2Me), 1625 (CO). ^{1}H-NMR: 3.64 (*s*, MeO); 3.74 (*s*, MeO); 5.61 (*s*, CHN); 6.98 (*d*, $^3J = 8.8$, 1 arom. H); 7.92 (*s*, 1 olef. H); 7.34–7.44 (*m*, 6 arom. H); 7.98 (*s*, 1 arom. H). ^{13}C-NMR: 51.93, 52.94 (2 MeO); 62.96 (CHN); 98.53 (C(4a)); 111.41 (C(3)); 118.59 (C(9)); 123.52 (C(5a)); 125.50 (C(6)); 126.42, 129.57, 128.37 (arom. CH); 130.99 (C(8)); 131.2 (C(7)); 132.73 (C(4)); 139.55 (arom. C); 151.49 (C(9a)); 159.49 (C(10a)); 169.57, 164.77 (2 CO_2Me); 171.35 (C(5)). EI-MS: 366 (83, $[M - CO_2Me]^+$), 367 (17), 258 (7), 230 (4), 77 (100, $C_6H_5^+$), 59 (25, CO_2Me^+). Anal. calc. for $C_{22}H_{16}ClNO_6$ (425.83): C 62.05, H 3.79, N 3.29; found: C 63.1, H 3.8, N 3.3.

*Diethyl 1,5-Dihydro-5-oxo-1-phenyl-2*H-*[1]benzopyrano[2,3-*b*]pyridine-2,3-dicarboxylate* (**6e**). Yield 0.403 g (96%). M.p. 190–191°. IR (KBr): 3050 (arom. C–H), 2950 (aliph. C–H), 1745 and 1700 (2 CO_2Et), 1625 (CO), 1500 (arom. C=C), 1215 (C–O). ^{1}H-NMR: 1.19 (*t*, $^3J = 7.1$, Me); 1.33 (*t*, $^3J = 7.1$, Me); 4.12–4.20 (*m*, CH_2O); 4.28 (*q*, $^3J = 7.1$, CH_2O); 5.64 (*s*, CHN); 7.1 (*d*, $^3J = 8.3$, 1 arom. H); 7.34 (*t*, $^3J = 7.4$, 1 arom. H); 7.38–7.51 (*m*, $^3J = 7.7$, 6 arom. H); 8.06 (*s*, 1 olef. H); 8.21 (*d*, $^3J = 1.2$, 1 arom. H). ^{13}C-NMR: 13.92 (Me); 14.31 (Me); 60.85 (CH_2O); 62.08 (CH_2O); 62.75 (CHN); 98.73 (C(4a)); 111.72 (C(3)); 116.97 (C(9)); 122.66 (C(5a)), 125.41 (C(6)), 125.59 (CH), 126.25 (C(7)), 126.59, 128.15, 129.49 (arom. CH), 130.92 (C(8)); 139.97 (arom. C); 153.34 (C(9a)); 159.75 (C(10a)); 164.74, 169.36 (2 CO_2Et); 172.92 (C(5)). EI-MS: 419 (1, M^+), 374 (1, $[M - OEt]^+$), 347 (26), 346 (100, $[M - CO_2Et]^+$), 318 (47, $[M - CO_2Et - C_2H_4]^+$), 196 (4, $[M - 2\ CO_2Et - Ph]^+$), 77 (51, $C_6H_5^+$), 59 (25, CO_2Me^+). Anal. calc. for $C_{24}H_{21}NO_6$ (419.44): C 68.73, H 5.05, N 3.34; found: C 69.1, H 5.1, N 3.4.

*Diethyl 1-(2-Ethoxy-2-oxoethyl)-1,5-dihydro-5-oxo-2*H-*[1]benzopyrano[2,3-*b*]pyridine-2,3-dicarboxylate* (**6f**). Yield 0.395 g (92%). M.p. 191–192°. IR (KBr): 3050 (arom. C–H), 2975, 2900 (aliph. C–H), 1745, 1725 (2 CO_2Et), 1625 (CO), 1500 (arom. C=C). ^{1}H-NMR: 1.17 (*t*, ^3J = 6.5, Me); 1.22 (*t*, ^3J = 6.5, Me); 1.27 (*t*, ^3J = 6.6, Me); 4.29 (*s*, CH_2N); 4.11 (*q*, ^3J = 6.3, CH_2O); 4.19 (*m*, 2 CH_2O); 5.30 (*s*, CHN); 7.61 (*t*, ^3J = 7.5, 1 arom. H); 7.39–7.54 (*m*, 2 arom. H); 7.96 (*s*, 1 olef. H); 8.11 (*d*, ^3J = 7.5, 1 arom. H). ^{13}C-NMR: 13.83, 14.20, 14.01 (3 Me); 49.56 (CH_2N); 60.68, 61.92, 61.43 (3 CH_2O); 62.04 (CHN); 96.88 (C(4a)); 111.32 (C(3)); 116.52 (C(9)); 122.46 (C(5a)); 125.52 (C(6)); 126.27 (C(7)); 130.98 (C(8)); 132.67 (C(4)); 153.01 (C(9a)); 160.34 (C(10a)); 164.77, 167.32, 168.70 (3 CO_2Et); 172.04 (C(5)). EI-MS: 429 (1, M^+), 384 (1, $[M - OEt]^+$), 357 (21, $[M + 1 - CO_2Et]^+$), 356 (100, $[M - CO_2Et]^+$), 328 (17, $[M - CO_2Et - C_2H_4]^+$), 300 (25), 283 (4, $[M - 2\ CO_2Et]^+$), 210 (7, $[M - 3\ CO_2Et]^+$), 196 (4, $[M - 2\ CO_2Et - CH_2CO_2Et]^+$). Anal. calc. for $C_{22}H_{23}NO_8$ (429.43): C 61.53, H 5.40, N 3.26; found: C 60.1, H 5.3, N 3.3.

*Diethyl 1,5-Dihydro-1-(2-methoxyphenyl)-5-oxo-2*H-*[1]benzopyrano[2,3-*b*]pyridine-2,3-dicarboxylate* (**6g**). Yield 0.427 g (95%). M.p. 178–180°. IR (KBr): 3050 (arom. C–H), 2900 (aliph. C–H), 1745, 1700 (2 CO_2Et), 1625 (CO), 1500 (arom. C=C), 1215 (C–O). ^{1}H-NMR: 1.15 (*t*, ^3J = 7.1, Me); 1.30 (*t*, ^3J = 7.1, Me); 3.73 (*s*, MeO); 4.11 (*m*, ^3J = 7.2, CH_2O); 4.24 (*q*, ^3J = 7.0, CH_2O); 5.52 (*s*, CHN); 6.67–7.04 (*m*, 3 arom. H); 7.28, 7.36, 7.44 (3*t*, ^3J = 8.02, 3 arom. H); 7.56 (*s*, arom. H); 8.06 (*s*, 1 olef. H); 8.16 (*d*, ^3J = 7.7, arom. H). ^{13}C-NMR: 13.88, 14.27 (2 Me); 55.77 (MeO); 61.77, 60.63 (2 CH_2O); 62.35 (CHN); 97.96 (C(4a)); 111.63 (C(3)); 112 (CH); 116.78 (C(9)); 120.80 (CH); 122.59 (C(5a)); 125.16 (C(6)); 126.14 (C(7)); 128.04 (CH); 129.48 (C); 129.75 (arom. CH); 130.9 (C(8)); 153.35 (C(9a)); 153.90 (arom. C); 160.27 (C(10a)); 169.52, 164.8 (2 CO_2Et); 172.75 (C(5)). EI-MS: 449 (1, M^+), 450 (0.6, $[M + 1]^+$), 404 (1, $[M - OEt]^+$), 377 (34, $[M + 1 - CO_2Et]^+$), 376 (100, $[M - CO_2Et]^+$), 349 (39), 348 (9), 332 (3), 304 (28), 288 (3). Anal. calc. for $C_{25}H_{23}NO_7$ (449.46): C 66.81, H 5.16, N 3.12; found: C 65.5, H 5.0, N 3.0.

*Diethyl 7-Chloro-1,5-dihydro-5-oxo-1-phenyl-2*H-*[1]benzopyrano[2,3-*b*]pyridine-2,3-dicarboxylate* (**6h**). Yield 0.433 g (95%). M.p. 195–196°. IR (KBr): 3070 (arom. C–H), 2975 (aliph. C–H), 1745, 1700 (2 CO_2Et), 1625 (CO), 1500 (arom. C=C), 1215 (C–O). ^{1}H-NMR: 1.17 (*t*, ^3J = 7.1, Me); 1.30 (*t*, ^3J = 7.1, Me); 4.13 (*m*, CH_2O); 4.25 (*q*, ^3J = 7.1, CH_2O); 5.61 (*s*, CHN); 7.02 (*d*, ^3J = 8.81, 1 arom. H); 7.37–7.46 (*m*, 6 arom. H); 7.98 (*s*, 1 olef. H); 8.09 (*d*, ^3J = 2.4, 1 arom. H). ^{13}C-NMR: 13.86 (Me); 14.24 (Me); 60.90 (CH_2O); 62.13 (CH_2O); 62.84 (CHN); 98.50 (C(4a)); 112.17 (C(3)); 118.56 (C(9)); 123.63 (C(5a)); 125.64 (C(6)); 126.55, 128.36, 129.55 (3 arom. CH); 130.52 (C(8)); 131.29 (C(7)); 132.73 (CH); 139.63 (arom. C); 151.52 (C(9a)); 159.74 (C(10a)); 169.13, 164.51 (2 CO_2Et); 171.55 (C(5)). EI-MS: 408 (1, $[M - OEt]^+$), 380 (100, $[M - CO_2Et]^+$), 381 (21), 352 (45). Anal. calc. for $C_{24}H_{20}ClNO_6$ (453.88): C 63.51, H 4.44, N 3.09; found: C 64.1, H 4.5, N 3.1.

REFERENCES

[1] P. Pohler, C. Tomm, *Tetrahedron Lett.* **1967**, 3479.
[2] W. T. L. Sidwel, C. Tomm, *Tetrahedron Lett.* **1970**, 475.
[3] B. Chenera, M. L. West, J. A. Finkelstein, G. B. Dreyer, *J. Org. Chem.* **1993**, *58*, 5605.
[4] V. Bangani, N. R. Crouch, D. A. Mulholland, *Phytochemistry* **1999**, *51*, 947.
[5] Z. Q. Xu, R. W. Bucheit, T. L. Stup, M. T. Flavin, A. Khilevich, J. D. Rezzo, L. Lin, D. E. Zembower, *Bioorg. Med. Chem. Lett.* **1998**, *8*, 2179.
[6] T. Ishakava, Y. Oku, T. Tanaka, T. Kumamoto, *Tetrahedron Lett.* **1999**, *40*, 3777.
[7] T. Al-Nakib, V. Bezjak, M. J. Meegan, R. Chandy, *Eur. J. Med. Chem.* **1990**, *25*, 455.
[8] K. I. Kataoka, T. Shiota, T. Takeyasu, T. Muchizuki, K. Taneda, M. Ota, H. Hanabe, Y. Yamaguchi, *J. Med. Chem.* **1995**, *38*, 3174.
[9] J. Kitajima, T. Ishikawa, Y. Tanaka, Y. Ida, *Chem. Pharm. Bull.* **1999**, *47*, 1448.
[10] J. B. Harborne, in 'The Flavanoids: Advances in Research Since 1986', Chapman & Hall, New York, 1986.
[11] M. Gill, in 'The Chemistry of Natural Products', 2nd edn., Ed. R. H. Thomson, Blackie, Surrey, 1993, p. 60.
[12] M. Negwer, 'Organic Chemical Drugs and their Synonyms', 7th edn., Akademie, Stuttgart, 1994.
[13] E. Muller, T. Kalai, J. Jeko, K. Hideg, *Synthesis* **2000**, 1415.

[14] C. K. Ghosh, C. Ghosh, *Indian J. Chem.*, *Sect. B* **1997**, *36*, 968.
[15] R. P. Hsung, *J. Org. Chem*. **1997**, *62*, 7904.
[16] C. K. Bandyopadhayay, R. Sur, R. Patra, A. Sen, *Tetrahedron* **2000**, *56*, 3583.
[17] J. A. Drewe, P. W. Groundwater, *J. Chem. Soc., Perkin Trans. 1* **1997**, 601.
[18] A. Boumendjel, F. Bois, C. Beney, A. M. Mariotte, G. Conseil, A. Di Petro, *Bioorg. Med. Chem. Lett*. **2001**, *11*, 75.
[19] R. Larget, B. Lockhart, P. Renard, M. Largeron, *Bioorg. Med. Chem. Lett*. **2000**, *10*, 835.
[20] A. Gross, D. R. Borcherding, D. Friedrich, J. S. Sabol, *Tetrahedron Lett*. **2001**, *42*, 1631.
[21] G. Singh, R. Singh, N. K. Girdhar, M. P. S. Ishar, *Tetrahedron* **2002**, *58*, 2471.
[22] G. Kolokythas, I. K. Kostakis, N. Pouli, P. Marakos, D. Keletsas, H. Pratsinis, *Bioorg. Med. Chem.* **2003**, *11*, 4591.
[23] M. Darbarwar, V. Sundaramurthy, *Synthesis* **1982**, 337.
[24] C. K. Ghosh, C. Bandyopadhyay, J. Maiti, *Heterocycles* **1987**, *26*, 1623.
[25] C. K. Ghosh, *J. Indian Chem. Soc*. **1990**, *67*, 5; C. K. Ghosh, *J. Indian Chem. Soc*. **1991**, *68*, 21, and refs. cit. therein.
[26] I. Sigg, G. Hass, T. Winkler, *Helv. Chim. Acta* **1982**, *65*, 275.
[27] C. Ghosh, N. Tewari, *J. Org. Chem*. **1980**, *45*, 1964.
[28] A. O. Fitton, P. G. Houghton, H. Suschitzky, *Synthesis* **1979**, 337.
[29] A. O. Fitton, M. Kosmirok, H. Suschitzky, J. L. Suschitzky, *Tetrahedron Lett*. **1982**, *23*, 3953.
[30] G. Singh, G. Singh, M. P. S. Ishar, *Synlett* **2003**, 256.
[31] C. Bandyopadhyay, K. R. Sur, R. Patra, S. Banerjee, *J. Chem. Res., Synop.* **2003**, 459.
[32] C. Bandyopadhyay, K. R. Sur, R. Patra, A. Sen, *Tetrahedron* **2000**, *56*, 3583.
[33] M. P. S. Ishar, R. Kumar, K. Singh, *Tetrahedron Lett.* **1998**, *39*, 6547.
[34] K. C. Nicolaou, M. W. Harter, J. L. Gunzner, A. Nadin, *Liebigs Ann. Recl*. **1997**, 1283.
[35] K. B. Becker, *Tetrahedron* **1980**, *36*, 1717; K. P. C. Vollhardt, *Synthesis* **1975**, 765.
[36] I. Yavari, M. Adib, *Tetrahedron* **2001**, *57*, 5873.
[37] I. Yavari, A. Mirzaei, L. Moradi, *Helv. Chim. Acta* **2006**, *89*, 2825.
[38] A. Alizadeh, H. Masrouri, S. Rostamnia, F. Movahedi, *Helv. Chim. Acta* **2006**, *89*, 923.
[39] A. Alizadeh, *Helv. Chim. Acta* **2005**, *88*, 304.

Received April 4, 2007