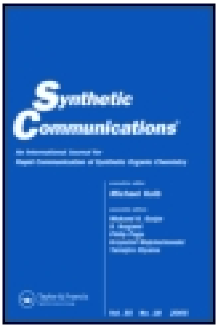

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Synthesis of 9, 10-Dihydro-9-hydroxy-2H,8H-benzo-[1,2-b:3,4-b']dipyran-2-ones

V. Satyanarayana [a], Ch. Prasad Rao [a], G. L. David Krupadanam [a] & G. Srimannarayana [a]

[a] Department of Chemistry, Osmania University, Hyderabad, 500 007, India

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SYNTHESIS OF 9,10-DIHYDRO-9-HYDROXY-2H,8H-BENZO-[1,2-b:3,4-b']DIPYRAN-2-ONES

V. Satyanarayana, Ch. Prasad Rao, G.L. David Krupadanam and
G. Srimannarayana*

Department of Chemistry, Osmania University,
Hyderabad 500 007, India

ABSTRACT: Oxidation of o-allyl-7-hydroxycoumarins with m-CPBA gave the corresponding 9,10-dihydro-9-hydroxy-2H,-8H-benzo [1,2-b:3,4-b']dipyran-2-ones.

In view of the interesting physiological properties of coumarins[1] we reported earlier the synthesis of several new pyrano and furanocoumarins by adopting new routes[2-4]. In this paper we report the results of the reaction of o-allyl-7-hydroxy-4-methylcoumarins (3a-e) with m-chloroperoxybenzoic acid (m-CPBA) to give the exclusively 9,10-dihydro-9-hydroxy-4-methyl-2H,8H-benzo [1,2-b:3,4-b'] dipyran-2-ones (4a-d & f). However, Murray et al.[5] reported that oxidation of osthenol (8- γ, γ -dimethylallyl-7-hydroxycoumarin) with m-CPBA furnished dihydrofuranocoumarin [(±) columbianetin] under neutral conditions and dihydropyranocoumarin [(±) lomatin] under acidic conditions.

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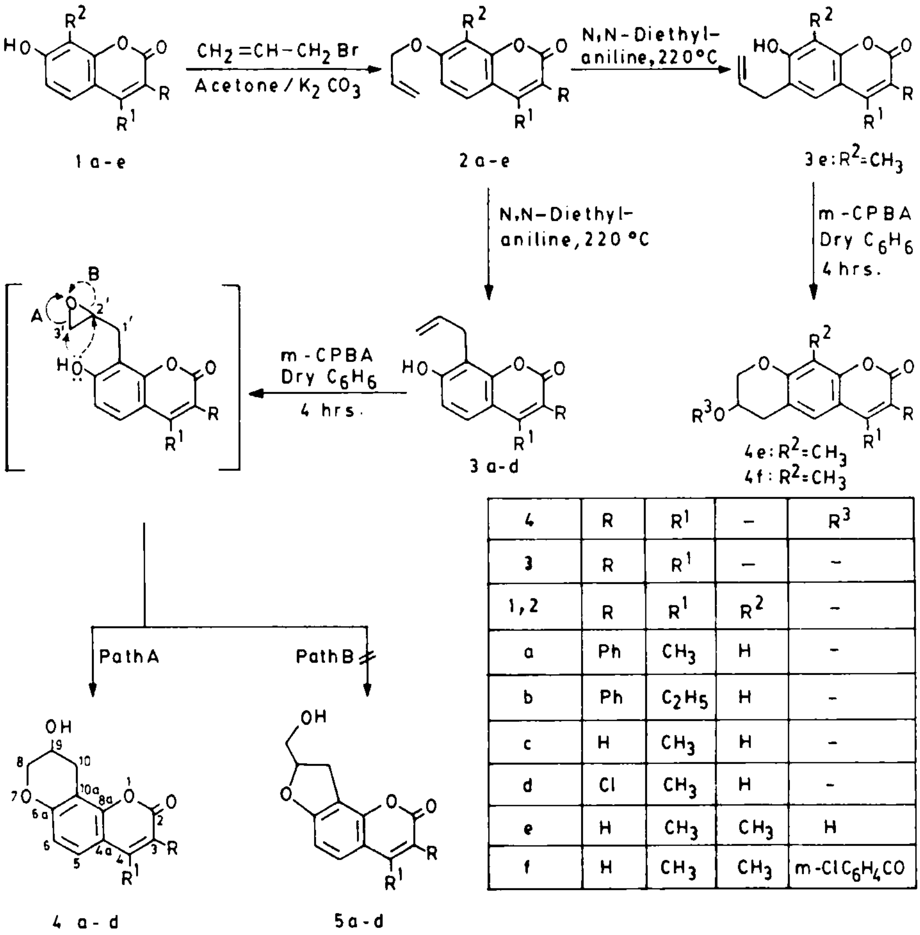
* To whom correspondence should be addressed.



4	R	R^1	–	R^3
3	R	R^1	–	–
1,2	R	R^1	R^2	–
a	Ph	CH_3	H	-
b	Ph	C_2H_5	H	-
c	H	CH_3	H	-
d	Cl	CH_3	H	-
e	H	CH_3	CH_3	H
f	H	CH_3	CH_3	m-ClC_6H_4CO

SCHEME-1

7-Hydroxycoumarins (1a-e) were allylated with allyl bromide to give corresponding 7-allyloxycoumarins (2a-e) in about 97% yield. These compounds, 2a-e on Claisen rearrangement in N,N-diethylaniline afford o-allyl-7-hydroxycoumarins (3a-e) in good yields (96%). The melting points and spectral data of 2a-e and 3a-e are in agreement with earlier reported data[2].

Table 1

Physical and spectral data of 4a-d & 4f

Compd.	Yield* (%)	m.p. °C	Molecular formula	IR(KBr) max cm^{-1}		UV λ_{max}^{MeOH} nm (log ε)	Mass data** (m/e)
				(C-H)	(C=O)		
4a	75	206	$C_{19}H_{16}O_4$	3500	1710	218 (4.63) 252 (3.87)sh 262 (3.80)sh 330 (4.40)	308 (M^+,100), 289 (25), 280 (60), 264 (25), 236 (80)
4b	75	188	$C_{20}H_{18}O_4$	3450	1705	218 (4.65) 250 (3.98)sh 263 (3.96)sh 330 (4.38)	322 (M^+, 100), 303 (15), 294 (60), 278 (20), 250 (60)
4c	73	123	$C_{13}H_{12}O_4$	3250	1705	218 (4.60) 250 (3.96)sh 262 (3.90) sh 330 (4.41)	232 (M^+, 100), 213 (15), 204 (50), 188 (15), 160 (40)
4d	72	200	$C_{13}H_{11}O_4Cl$	3400	1710	218 (4.59) 252 (3.97)sh 260 (3.91)sh 330 (4.41)	266 (M^+, 100), 247 (25), 238 (55), 222 (15), 194 (45)
4f	52	197	$C_{21}H_{17}O_5Cl$	3200	1740 1710	218 (4.57) 248 (3.99)sh 260 (3.98)sh 330 (4.38)	384 (M^+, 2), 246 (100), 218 (50), 202 (20), 174 (50), 141 (20), 139 (45), 113 (15), 111 (25)

* Recrystallised from methanol. All products gave satisfactory elemental analysis.

** Ionisation was carried out at 70 eV by electron impact, samples were introduced directly. Prominent peaks mentioned

Table 2

^{1}H-NMR spectral data of 4a-d (300 MHz, DMSO-D_6) and 4f (90 MHz, DMSO-D_6), (δ) ppm, J in Hz

Compd.	C_3-Sub.	C_4-Sub.	C_5-H	C_6-H	C_8-methylene protons		C_9-H	C_9-OH	C_{10}-methylene protons	
					C_8-H_{ax}	C_8-H_{eq}			$C_{10}H_{ax}$	C_{10}-H_{eq}
4a	C_6H_5 7.40 m,5H	CH_3 2.23 s,3H	7.64 d,1H $J_{5H,6H}$=8.60	6.88 d,1H $J_{6H,5H}$=8.60	3.63 dd,1H_{ax} $J_{8H_{ax},8H_{eq}}$=11.44 $J_{8H_{ax},9H}$=6.61	3.79 dd,1H_{eq} $J_{8H_{eq},8H_{ax}}$=11.44 $J_{8H_{eq},9H}$=3.32	5.23 m,1H	2.02 brs,1H	3.16 dd,1H_{ax} $J_{10H_{ax},10H_{eq}}$=15.94 $J_{10H_{ax},9H}$=6.96	3.39 dd,1H_{eq} $J_{10H_{eq},10H_{ax}}$=15.94 $J_{10H_{eq},9H}$=9.63
4b	C_6H_5 7.36 m,5H	CH_2-CH_3 1.13 t,3H 2.63 q,2H	7.65 d,1H $J_{5H,6H}$=8.74	6.84 d,1H $J_{6H,5H}$=8.74	3.72 dd,1H_{ax} $J_{8H_{ax},8H_{eq}}$=11.83 $J_{8H_{ax},9H}$=5.66	3.82 dd,1H_{eq} $J_{8H_{eq},8H_{ax}}$=11.83 $J_{8H_{eq},9H}$=2.96	5.07 m,1H	1.93 brs,1H	3.21 dd,1H_{ax} $J_{10H_{ax},10H_{eq}}$=16.07 $J_{10H_{ax},9H}$=7.22	3.42 dd,1H_{eq} $J_{10H_{eq},10H_{ax}}$=16.07 $J_{10H_{eq},9H}$=9.98
4c	6.12 s,1H	CH_3 2.35 s,3H	7.50 d,1H $J_{5H,6H}$=7.88	6.93 d,1H $J_{6H,5H}$=7.88	3.64 dd,1H_{ax} $J_{8H_{ax},8H_{eq}}$=11.48 $J_{8H_{ax},9H}$=5.86	3.82 dd,1H_{eq} $J_{8H_{eq},8H_{ax}}$=11.48 $J_{8H_{eq},9H}$=3.21	5.16 m,1H	1.88 brs,1H	3.08 dd,1H_{ax} $J_{10H_{ax},10H_{eq}}$=16.14 $J_{10H_{ax},9H}$=7.09	3.38 dd,1H_{eq} $J_{10H_{eq},10H_{ax}}$=16.14 $J_{10H_{eq},9H}$=9.87
4d	Cl	CH_3 2.41 s,3H	7.51 d,1H $J_{5H,6H}$=7.86	7.14 d,1H $J_{6H,5H}$=7.86	3.61 m,1H_{ax}	3.88 m,1H_{eq}	5.12 m,1H	2.14 brs,1H	3.10 m,1H_{ax}	3.27 m,1H_{eq}
	C_3-H	C_4-CH_3	C_5-H	C_{10}-CH_3	C_6methylene protons		C_7-H		C_8-methylene protons	
4f	6.08 s,1H	CH_3 2.29 s,3H	mix. with aromatic protons	CH_3 2.48 s,3H	3.81 m,2H (6 - H_{ax} & 6 - H_{eq})		5.01 m,1H		3.33 m, 2H (8 - H_{ax} & 8 - H_{eq})	

Aromatic protons : 7.28-7.81 m,5H (5-H, 2'-H, 4'-H, 5'-H and 6'-H)

Equimolar amounts of 8-allyl-7-hydroxy-4-methyl-3-phenylcoumarin (3a) and m-chloroperoxybenzoic acid were dissolved in dry benzene and refluxed for 4 hrs. Work up of the reaction mixture gave a semi-solid, which was chromatographed over a column of silica gel using benzene:chloroform (1:1 v/v) to give 9,10-dihydro-9-hydroxy-4-methyl-3-phenyl-2H,8H-benzo [1,2-b:3,4-b'] dipyran-2-one (4a), m.p. 206°C; IR(KBr) 3500 cm^{-1} (OH), 1710 cm^{-1} (C=O). Its PMR (300 MHz, DMSO-d_6) spectrum showed a signal pattern characteristic of -O-CH_2-CHOH-CH_2- as a part of a ring system. The C_8-axial and C_8-equitorial protons resonated at δ 3.63 ($J_{8H_{ax}8H_{eq}}$ = 11.44 Hz; $J_{8H_{ax},9H}$= 6.61 Hz) and 3.79 ($J_{8H_{eq},8H_{ax}}$ = 11.44 Hz; $J_{8H_{eq},9H}$ = 3.32 Hz), respectively, as two double doublets. The C-9 proton resonated at δ 5.23 as a complex multiplet and the C_9-OH resonated as a broad singlet at δ 2.02. The C_{10}-axial and C_{10}-equitorial protons resonated at δ 3.16 ($J_{10H_{ax},10H_{eq}}$ = 15.94 Hz; $J_{10H_{ax},9H}$ = 6.96 Hz) and 3.39 ($J_{10H_{eq},10H_{ax}}$ = 15.94 Hz; $J_{10H_{eq},9H}$ = 9.63 Hz), respectively, as two double doublets. The resonances due to the coumarin ring appeared at their expected positions (Table 2).

In MS, in addition to the peaks characteristic of the coumarin ring system, 4a also showed M-1-18 [M-(H+H_2O)] (pyrelium ion), M-44 [M-C_2H_4O], M-28-44 [M-(CO+C_2H_4O)] . These peaks are characteristic of the newly formed 9,10-dihydro-9-hydroxy-4-methyl-3-phenyl-2H,8H-benzo [1,2-b:3,4-b'] dipyran-2-one (4a) system. The completely decoupled ^{13}C-NMR spectrum of 4a, also supports the structure assigned to 4a. The carbon resonances due to the hydroxy dihydropyran unit, -O-CH_2-CHOH-CH_2- appeared at 62.17, 84.85 and 26.95 ppm respectively. In the off resonance decoupled spectrum the C-8 appeared as a triplet, C-9 as a doublet and C-10 as a triplet. Similarly, compounds 3b-d were subjected to m-CPBA oxidation to yield angularly fused dihydropyranocoumarins, 4b-d and their characterisation data are given in Tables 1 & 2. In the m-CPBA oxidation of 3e, the product of the reaction was identified as 7,8-dihydro-4,10-dimethyl-2-oxo-2H,6H-benzo [1,2-b:5,4-b'] dipyran-7-yl-3-chlorobenzoate (4f), instead of (4e).

The regioselective formation of 9,10-dihydro-9-hydroxy-2H,8H-benzo [1,2-b:3,4-b'] dipyran-2-ones (4a-d) is explained by considering initial formation of an epoxide. Intramolecular attack of the epoxide by the adjacent phenolic OH may be either at C-3' to give 4a-d or at C-2' to give (5a-d). Since the C-3' position is sterically less hindered than C-2', the phenolic OH attacks C-3' of the epoxide to give 4a-d exclusively[6] (Scheme 1).

EXPERIMENTAL

The compounds 1a[7], 1b[7], 1c[8], 1d[9] and 1e[10] were prepared as per the procedures reported in literature. These compounds were successively allylated to give 2a[7], 2b[7], 2c[11], 2d[2] and 2e[12]. The Claisen rearrangement of 2a-e furnished 3a[2], 3b, 3c[11], 3d[2] and 3e[12], respectively.

Typical procedure for 9,10-dihydro-9-hydroxy-4-methyl-3-phenyl-2H,8H-benzo [1,2-b:3,4-b']dipyran-2-one (4a)

8-Allyl-7-hydroxy-4-methyl-3-phenylcoumarin (3a) (1 mmol) and m-chloroperoxybenzoic acid (1 mmol) were dissolved in dry benzene (100 ml) and refluxed for 4 hrs on a water bath. After cooling to room temperature, the separated m-chlorobenzoic acid was removed by filtration and the benzene solution was washed with 2% aq.sodium bicarbonate (2 x 50 ml, to remove traces of acid), with water, and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the product thus obtained was subjected to column chromatography over silica gel (30 g, ACME, 200 mesh). Elution with benzene-chloroform (1:1 v/v) (200 ml) gave 4a which was crystallised from methanol as colourless crystals (0.45 g, 75% yield), m.p. 206°C. ^{13}C-NMR (DMSO-d_6; 22.63 MHz; fully decoulpled): δ 162.45 (C-2), 121.64 (C-3), 147.63 (C-4), 112.28 (C-4a), 129.44 (C-5), 112.86 (C-6), 159.14 (C-6a), 105.39 (C-10a), 148.67 (C-8a), 134.18 (C-1'), 127.23 (C-2' & C-6'), 126.77 (C-3' & C-5'), 125.60 (C-4'), 15.57 (C_4-CH_3), 62.17 (C-8), 84.85 (C-9), 26.95 (C-10).

Compounds 4b-d and 4f were prepared similarly by the above procedure and their characterisation data are given in Tables 1 & 2.

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