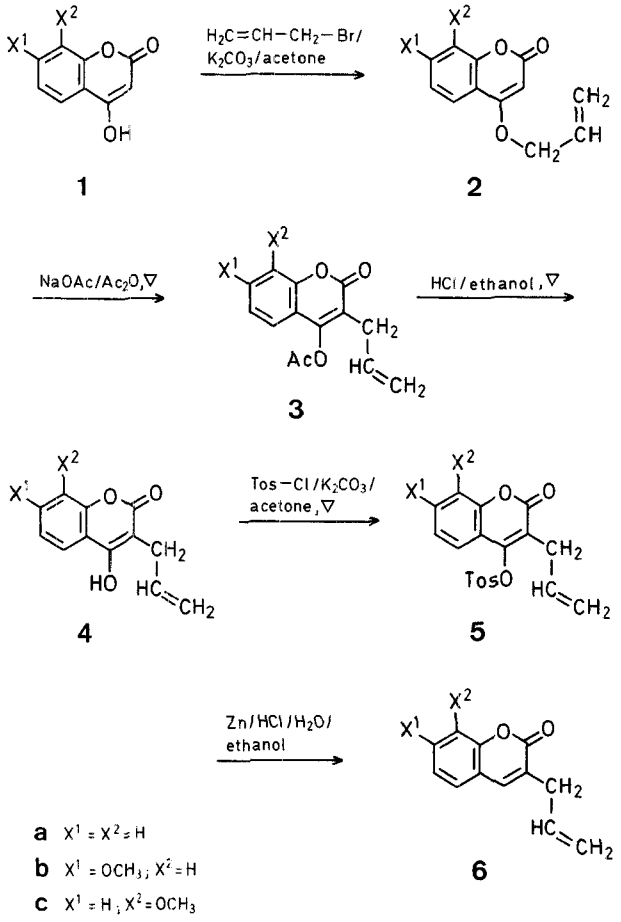

The conversion of 4-hydroxycoumarins (**1**) into 3-allyl-4-hydroxycoumarins (**4**) cannot be accomplished via direct Claisen rearrangement of 4-allyloxycoumarins (**2**); the attempted rearrangement in *N,N*-dimethylaniline or at reduced pressure lead only to cyclization[7]. We have now found that the rearrangement of **2** (obtained from **1** and allyl bromide in the presence of potassium carbonate[7]) can be achieved in acetic anhydride in the presence of sodium acetate to give the corresponding 4-acetoxy-3-allylcoumarins (**3**); these compounds are readily hydrolyzed to the 3-allyl-4-hydroxycoumarins (**4**). [3-Alkenyl-4-hydroxycoumarins of the type **4** are known to possess anticoagulant activity[8] and they are essential intermediates for the synthesis of naturally occurring furo[3,2-*c*]coumarins[9,10].]

The 3-allyl-4-hydroxycoumarins **4** are *O*-tosylated using tosyl chloride/potassium carbonate in acetone to give 3-allyl-4-tosyloxycoumarins (**5**) which are reductively detosylated with zinc/hydrochloric acid to afford the desired 3-allylcoumarins (**6**).

The structure of compounds **2**, **4**, **5**, and **6** were confirmed by microanalyses, I.R.-, and ^{1}H-N.M.R.-spectral data.

A Facile Synthesis of 3-Allylcoumarins

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3-Alkenylcoumarins have been isolated from natural products[1,2,3]; however, a convenient method for their synthesis has hitherto not been described although a number of methods are available for the synthesis of their saturated analogs, 3-alkylcoumarins[4,5]. Only 3-(1,1-dimethylallyl)-7-hydroxy-6-methoxycoumarin has been obtained in small quantities as an abnormal product from the Claisen rearrangement of 6-methoxy-7-*O*-(3-methyl-2-butenyl)-coumarin[6]. We describe now a convenient synthetic route to 3-allylcoumarins (**6**) starting from 4-hydroxycoumarins (**1**) via 3-allyl-4-hydroxycoumarins (**4**).

3-Allylcoumarins (6) from 4-Hydroxycoumarins (1); General Procedure:

4-Allyloxycoumarins (**2**): These compounds are prepared from 4-hydroxycoumarins (**1**) as described in Ref. [7].

4-Acetoxy-3-allylcoumarins (**3**): A mixture of the 4-allyloxycoumarin (**2**; 1 g), acetic anhydride (15 ml), and fused sodium acetate (1 g) is refluxed for 2 h and then poured onto crushed ice (30 g). The resultant solid product is isolated by suction, washed with water, and recrystallized from methanol.

3-Allyl-4-hydroxycoumarins (**4**): The 4-acetoxy-3-allylcoumarin (**3**; 1 g) is dissolved in ethanol (15 ml), conc. hydrochloric acid (5 ml) is

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Table 1. 4-Acetoxy-3-allylcoumarins (**3**)

3	X^1	X^2	Yield [%]	m.p.	Molecular formula[a]	I.R. (KBr) ν [cm^{-1}]	^{1}H-N.M.R. ($CDCl_3$/TMS) δ [ppm]
a	H	H	70	82–83 °C	$C_{14}H_{12}O_4$ (244.2)	1770 ($OCOCH_3$); 1710 (C=O); 1605 (C=C)	2.42 (s, 3H, OAc); 3.20 (d, 2H, J=6 Hz, CH_2–CH=CH_2); 4.92 (m, 2H, CH_2–CH=CH_2); 5.52 (m, 1H, CH_2–CH–CH_2); 7.46 (m, 4H, 5-H, 6-H, 7-H, 8-H)
b	OCH_3	H	75	87–88 °C	$C_{15}H_{14}O_5$ (274.3)	1765 ($OCOCH_3$); 1715 (C=O); 1610 (C=C)	2.40 (s, 3H, OAc); 3.22 (d, 2H, J=6 Hz, CH_2–CH=CH_2); 3.86 (s, 3H, OCH_3); 5.02 (m, 2H, CH_2–CH=CH_2); 5.65 (m, 1H, CH_2–CH–CH_2); 6.80 (d, 1H, J=2 Hz, 8-H); 6.85 (dd, 1H, J=2 Hz, J=9 Hz, 6-H); 7.25 (d, 1H, J=9 Hz, 5-H)
c	OCH_3	OCH_3	82	96–97 °C	$C_{16}H_{16}O_6$ (304.3)	1760 ($OCOCH_3$); 1715 (C=O); 1610, 1600 (C=C)	2.40 (s, 3H, OAc); 3.20 (d, 2H, J=6 Hz, CH_2–CH–CH_2); 3.92, 4.0 (each s, each 3H, 7- and 8-OCH_3); 5.10 (m, 2H, CH_2–CH=CH_2); 5.62 (m, 1H, CH_2–CH–CH_2); 6.90 (d, 1H, J=9.5 Hz, 6-H); 7.40 (d, 1H, J=9.5 Hz, 5-H)

[a] The microanalyses were in satisfactory agreement with the calculated values: C, ±0.21; H, ±0.22.

Table 2. 3-Allyl-4-hydroxycoumarins (**4**)

4	X^1	X^2	Yield [%]	m.p.	m.p. reported	I.R. (KBr) ν [cm^{-1}]
a	H	H	60	139–140 °C	139–140 °C	3300 (OH); 1690 (C=O); 1600 (C=C)
b	OCH_3	H	60	187–188 °C	187–188 °C	3320 (OH); 1680 (C=O); 1600 (C=C)
c	OCH_3	OCH_3	70	157–158 °C	152–155 °C	3350 (OH); 1675 (C=O); 1605 (C=C)

Table 3. 3-Allyl-4-tosyloxycoumarins (**5**)

5	X^1	X^2	Yield [%]	m.p.	Molecular formula[a]	I.R. (KBr) ν [cm^{-1}]	^{1}H-N.M.R. ($CDCl_3$/TMS) δ [ppm]
a	H	H	70	120–121 °C	$C_{19}H_{16}O_5S$ (356.3)	1705 (C=O); 1610, 1600 (C=C)	2.48 (s, 3H, C_6H_4–CH_3); 3.16 (d, 2H, J=6 Hz, CH_2–CH–CH_2); 5.0 (m, 2H, CH_2–CH=CH_2); 5.65 (m, 1H, CH_2–CH–CH_2); 7.28, 7.85 (each d, each 2H, J=9.5 Hz each, C_6H_4–CH_3); 7.40 (m, 4H, 5-H, 6-H, 7-H, 8-H)
b	OCH_3	H	70	130–132 °C	$C_{20}H_{18}O_6S$ (386.4)	1710 (C=O); 1615, 1605 (C=C)	2.52 (s, 3H, C_6H_4–CH_3); 3.16 (d, 2H, J=6 Hz, CH_2–CH–CH_2); 3.88 (s, 3H, OCH_3); 5.05 (m, 2H, CH_2–CH=CH_2); 5.72 (m, 1H, CH_2–CH–CH_2); 6.75 (dd, 1H, J=2 Hz; J=9 Hz, 6-H); 6.82 (d, 1H, J=2 Hz, 8-H); 7.26 (d, 1H, J=9 Hz, 5-H); 7.42, 7.82 (each d, each 2H, J=9 Hz, C_6H_4–CH_3)
c	OCH_3	OCH_3	75	133–135 °C	$C_{21}H_{20}O_7S$ (412.4)	1710 (C=O); 1610, 1600 (C=C)	2.60 (s, 3H, C_6H_4–CH_3); 3.22 (d, 2H, J=6 Hz, CH_2–CH=CH_2); 4.10, 4.15 (each s, each 3H, 7-OCH_3, 8-OCH_3); 5.14 (m, 2H, CH_2–CH–CH_2); 5.80 (m, 1H, CH_2–CH–CH_2); 6.92 (d, 1H, J=9.5 Hz, 6-H); 7.40 (d, 1H, J=9.5 Hz, 5-H); 7.44, 7.84 (each d, each 2H, J=9 Hz, C_6H_4–CH_3)

[a] The microanalyses were in satisfactory agreement with the calculated values: C, ±0.18; H, ±0.18.

added, and the mixture is refluxed for 30 min. It is then allowed to cool and the product **4** isolated by suction, washed with water, and recrystallized from methanol.

3-Allyl-4-tosyloxycoumarins (**5**): A mixture of the 3-allyl-4-hydroxycoumarin (**4**; 0.01 mol), acetone (50 ml), tosyl chloride (1.91 g, 0.01 mol), and potassium carbonate (2 g) is refluxed for 4 h. The inorganic salts are filtered off and washed with acetone and the combined filtrates are evaporated in vacuo to give product **5**.

3-Allylcoumarins (**6**): The 3-allyl-4-tosyloxycoumarin (**5**; 1 g) is dissolved in ethanol (25 ml) and zinc (3 g) is added. Then, conc. hydrochloric acid (10 ml) is added, the mixture refluxed for 1 h, and then poured onto crushed ice (30 g). The resultant solid product is isolated by suction, washed with water, dried, and recrystallized from benzene/petroleum ether.

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Table 4. 3-Allylcoumarins (**6**)

6	X¹	X²	Yield [%]	m.p.	Molecular formula[a]	I.R. (KBr) ν [cm^{-1}]	^{1}H-N.M.R. ($CDCl_3$/TMS) δ [ppm]
a	H	H	48	110–111 °C	$C_{12}H_{10}O_2$ (186.2)	1710 (C=O); 1610, 1600 (C=C)	3.20 (d, 2H, J=6 Hz, $-CH_2-CH=CH_2$); 5.10 (m, 2H, $-CH_2-CH=CH_2$); 5.82 (m, 1H, $-CH_2-CH-CH_2$); 7.20 (m, 4H, 5-H, 6-H, 7-H, 8-H); 7.72 (s, 1H, 4-H)
b	OCH_3	H	50	124–125 °C	$C_{13}H_{12}O_3$ (216.2)	1715 (C=O); 1610, 1600 (C=C)	3.20 (d, 2H, J=6 Hz, $-CH_2-CH-CH_2$); 3.90 (s, 3H, $-OCH_3$); 5.10 (m, 2H, $-CH_2-CH=CH_2$); 5.88 (m, 1H, $-CH_2-CH=CH_2$); 6.78 (dd, 1H, J=2 Hz, J=9 Hz, 6-H); 6.86 (d, 1H, J=2 Hz, 8-H); 7.70 (s, 1H, 4-H); 7.78 (d, 1H, J=9 Hz, 5-H)
c	OCH_3	OCH_3	54	90–91 °C	$C_{14}H_{14}O_4$ (246.2)	1715 (C=O); 1605, 1600 (C=C)	3.30 (d, 2H, J=6 Hz, $-CH_2-CH=CH_2$); 4.08 (s, 6H, 7- and 8-OCH_3); 5.25 (m, 2H, $-CH_2-CH=CH_2$); 6.82 (m, 1H, $-CH_2-CH-CH_2$); 6.90 (d, 1H, J=9.5 Hz, 6-H); 7.62 (s, 1H, 4-H); 7.82 (d, 1H, J=9.5 Hz, 5-H)

[a] The microanalyses were in satisfactory agreement with the calculated values: C, ±0.16; H, ±0.24.

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