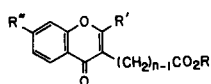


ω -(3-Chromonyl)alkanoic AcidsSeiji Yamaguchi*, Masao Mutoh, Masaaki Shimakura, Kunihiro Tsuzuki and
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Some ω -(3-chromonyl)alkanoic acid derivatives, **1a** and **2a**, $n = 4, 5$; **3a**, **4a** and **5a**, $n = 2-6$, were synthesized by cyclization of corresponding methyl ω -(2-hydroxybenzoyl)alkanoates **7b** or ethyl ω -(2,4-dihydroxybenzoyl)alkanoates **8b** with *N,N*-dimethylformamide-dimethyl acetal or acetic anhydride-DBU followed by hydrolysis.

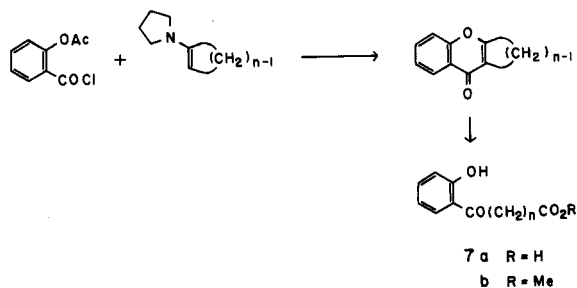
J. Heterocyclic Chem., **28**, 119 (1991).

In our studies on *O*-heterocyclic compounds, some carboxylic acid derivatives showed antimicrobial activities. So, we planned the syntheses of some fatty acid having an *O*-heterocycles in their terminal positions to test their antimicrobial activities. In this paper, we will report the synthesis of some ω -(3-chromonyl)alkanoic acids.

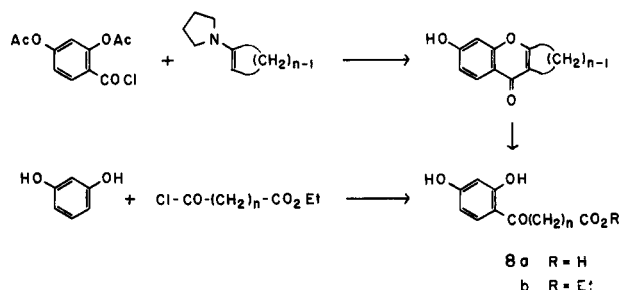


- 1 R'' = R' = H
 2 R'' = Me, R' = H
 3 R'' = H, R' = OH
 4 R'' = H, R' = OMe
 5 R'' = Me, R' = OH
 6 R'' = Me, R' = OAc

We planned the synthesis of the title compounds from ω -(2-hydroxybenzoyl)alkanoic acids **7a**. Some ω -(2-hydroxybenzoyl)alkanoic acids **7a**, $n = 4, 5$, were already reported by Hall and Plant [1], they prepared them by acylation of cyclopentanone or cyclohexanone-pyrrolidine enamine with 2-acetoxybenzoyl chloride followed by alkaline cleavage. Similarly, 6-(2,4-dihydroxybenzoyl)hexanoic acid **8a**, $n = 5$ was prepared from cyclohexanone-pyrrolidine enamine and 2,4-diacetoxybenzoyl chloride. However, 5-(2,4-dihydroxybenzoyl)pentanoic acid **8a**, $n = 5$ was not prepared in this procedure because of the low yield of its intermediate, 6-acetoxy-9*H*-cyclopenteno[*b*]chromen-9-one. Some ω -(2,4-dihydroxybenzoyl)alkanoic acids **8a**, $n = 2-6$, were also prepared by another procedure such as the



Friedel-Crafts acylation of resorcinol with succinic anhydride, glutaric anhydride, or the corresponding ω -ethoxycarbonylalkanoyl chlorides. These acids **7a** and **8a** were converted to their methyl esters **7b** or ethyl esters **8b**.



The cyclization of methyl esters **7b**, $n = 4, 5$ with ethyl formate-sodium metal gave a mixture of the corresponding ω -(3-chromonyl)alkanoic acids **1b**, $n = 4, 5$ and its methyl esters **1b**, $n = 4, 5$, and the cyclization of **7b**, $n = 4, 5$ with acetic anhydride-sodium acetate or DBU

Table 1
Cyclizations of Keto Esters to Chromones

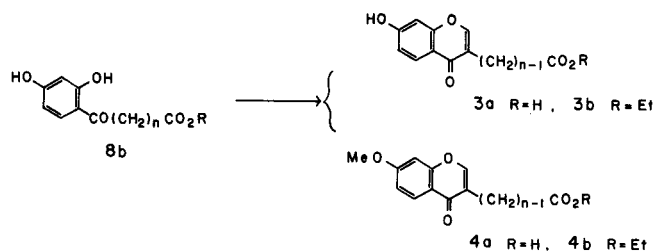
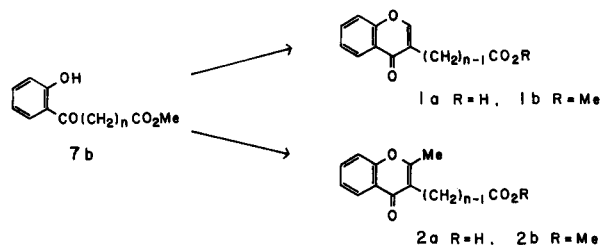
Starting Keto Esters	Cyclization Procedure	Chromones (Yield)
7b $n = 4$	HCO ₂ Et-Na	1a (17%) + 1b (40%)
7b $n = 5$	HCO ₂ Et-Na	1a (36%) + 1b (35%)
7b $n = 4$	Ac ₂ O-AcONa	2a (11%) + 2b (39%)
7b $n = 5$	Ac ₂ O-AcONa	2a (7%) + 2b (44%)
7b $n = 4$	Ac ₂ O-DBU	2a (34%) + 2b (19%)
7b $n = 5$	Ac ₂ O-DBU	2a (55%) + 2b (6%)
8b $n = 2$	DMF acetal	-----
8b $n = 3$	DMF acetal	3b (19%) + 4b (15%)
8b $n = 4$	DMF acetal	3b (15%) + 4b (21%)
8b $n = 5$	DMF acetal	3b (14%) + 4b (17%)
8b $n = 6$	DMF acetal	3b (10%) + 4b (10%)
8b $n = 2$	Ac ₂ O-DBU	5a (trace) + 6 (33%)
8b $n = 3$	Ac ₂ O-DBU	5a (3%) + 6 (64%)
8b $n = 4$	Ac ₂ O-DBU	5a (17%) + 6 (14%)
8b $n = 5$	Ac ₂ O-DBU	5b (13%) + 6 (48%)
8b $n = 6$	Ac ₂ O-DBU	5a (6%) + 6 (42%)

Table 2
Some Physical Data and Elemental Analyses of New Chromones

Compound	Melting point (°C)	ν CO (cm ⁻¹)	Mass M ⁺ (m/z)	Elemental Analyses			
				Found		Calcd.	
				C (%)	H (%)	C (%)	H (%)
1a n = 4	134.5-135.5	1725, 1640	232	67.15	5.23	64.23	5.21 for C ₁₃ H ₁₂ O ₄
1a n = 5	154-155	1700, 1635	246	68.03	5.65	68.28	5.73 for C ₁₄ H ₁₄ O ₄
1b n = 4	63-64	1725, 1645	246	68.47	5.78	68.28	5.73 for C ₁₄ H ₁₄ O ₄
1b n = 5	57-58	1725, 1645	260	69.39	6.27	69.21	6.20 for C ₁₅ H ₁₆ O ₄
2a n = 4	135-136	1725, 1625	246	68.54	6.53	68.28	5.73 for C ₁₄ H ₁₄ O ₄
2a n = 5	116.5-117.5	1730, 1630	260	69.49	6.41	69.21	6.20 for C ₁₅ H ₁₆ O ₄
2b n = 4	170-176 (2 mm Hg) [a]	1735, 1640	260	69.20	6.11	69.21	6.20 for C ₁₅ H ₁₆ O ₄
2b n = 5	ca. 230 (2 mm Hg) [a]	1735, 1635	274	69.92	6.90	70.05	6.61 for C ₁₆ H ₁₈ O ₄
3a n = 3	276-277	1700, 1630	234	61.60	4.01	61.54	4.30 for C ₁₂ H ₁₀ O ₅
3a n = 4	218.5-220	1705, 1635	248	62.64	4.99	62.90	4.87 for C ₁₃ H ₁₂ O ₅
3a n = 5	254-255	1700, 1630	262	64.34	5.52	64.11	5.38 for C ₁₄ H ₁₄ O ₅
3a n = 6	194-195	1710, 1630	276	65.00	5.59	65.21	5.84 for C ₁₅ H ₁₆ O ₅
3b n = 3	146-147	1725, 1635	262	63.99	5.10	64.11	5.38 for C ₁₄ H ₁₄ O ₅
3b n = 4	134.5-135.5	1735, 1640	276	65.30	5.59	65.21	5.84 for C ₁₅ H ₁₆ O ₅
3b n = 5	146-147	1720, 1635	290	66.11	6.04	66.19	6.25 for C ₁₆ H ₁₈ O ₅
3b n = 6	94-95	1735, 1640	304	67.05	6.45	67.09	6.62 for C ₁₇ H ₂₀ O ₅
4a n = 3	168.5-169.5	1725, 1630	248	62.75	4.75	62.90	4.87 for C ₁₃ H ₁₂ O ₅
4a n = 4	164-165	1700, 1630	262	64.13	5.46	64.11	5.38 for C ₁₄ H ₁₄ O ₅
4a n = 5	138-139	1715, 1625	276	64.95	5.83	65.21	5.84 for C ₁₅ H ₁₆ O ₅
4a n = 6	124-125	1720, 1635	290	66.24	6.13	66.19	6.25 for C ₁₆ H ₁₈ O ₅
4b n = 3	78.5-79.5	1725, 1635	276	65.08	5.74	65.21	5.84 for C ₁₅ H ₁₆ O ₅
4b n = 4	97-98	1725, 1630	290	66.45	6.25	66.19	6.25 for C ₁₆ H ₁₈ O ₅
4b n = 5	68-69	1730, 1630	304	66.96	6.62	67.09	6.62 for C ₁₇ H ₂₀ O ₅
4b n = 6	49-50	1725, 1630	318	68.08	7.24	67.91	6.97 for C ₁₈ H ₂₂ O ₅
5a n = 2	272-274	1710, 1635	234	61.46	4.57	61.54	4.30 for C ₁₂ H ₁₀ O ₅
5a n = 3	238-239.5	1695, 1625	248	62.67	4.90	62.90	4.87 for C ₁₃ H ₁₂ O ₅
5a n = 4	238.5-238.5	1730, 1630	262	63.99	5.09	64.11	5.38 for C ₁₄ H ₁₄ O ₅
5a n = 5	208-210	1705, 1635	276	64.98	5.92	65.21	5.84 for C ₁₅ H ₁₆ O ₅
5a n = 6	191-192	1710, 1630	290	66.11	6.32	66.19	6.25 for C ₁₆ H ₁₈ O ₅
5b n = 5	135.5-136.5	1735, 1640	304	67.10	6.61	67.09	6.62 for C ₁₇ H ₂₀ O ₅
6 n = 2	61-63	1760, 1730, 1640	304	62.88	5.49	63.15	5.30 for C ₁₆ H ₁₆ O ₆
6 n = 3	87-89	1760, 1730, 1640	318	64.04	5.65	64.14	5.70 for C ₁₇ H ₁₈ O ₆
6 n = 4	76-77	1765, 1735, 1635	332	64.97	6.12	65.05	6.07 for C ₁₈ H ₂₀ O ₆
6 n = 5	70.5-71.5	1760, 1740, 1650	346	65.61	6.67	65.88	6.40 for C ₁₉ H ₂₂ O ₆
6 n = 6	69-70	1760, 1735, 1640	360	66.92	6.72	66.65	6.71 for C ₂₀ H ₂₄ O ₆

[a] Boiling Point.

(1,8-diazabicyclo[5,4,0]-7-undecene) also gave a mixture of corresponding ω -(2-methyl-3-chromonyl)alkanoic acids **2a**, n = 4, 5 and its methyl esters **2b**, n = 4, 5. These results were summarized in Table 1. Similar cyclization of ethyl ω -(2,4-dihydroxybenzoyl)alkanoates **8b**, n = 3-6 with



DMF-dimethyl acetal gave a mixture of corresponding ω -(7-hydroxy-3-chromonyl)alkanoic acids **3a**, n = 3-6 and its methyl ethers **4b**, n = 3-6 and the cyclization of **8b**, n = 2-6 with acetic anhydride-DBU gave a mixture of corresponding ω -(7-hydroxy-2-methyl-3-chromonyl)alkanoic acids **5a**, n = 2-6 or its ethyl ester **5b**, n = 5 and ethyl

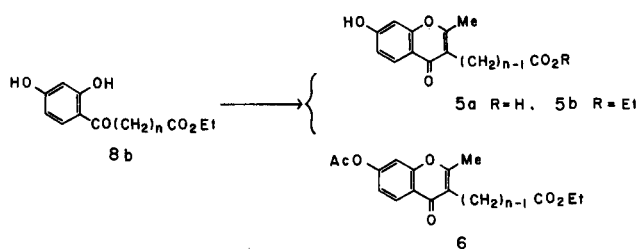
Table 3
PMR Data of New Chromones: δ /ppm (J/Hz)

Chromone	Solvent	Side methylenes α and ω others	2-R'	5-H	6-H	7-R''	8-H	R (Ester)
1a n = 4	DMSO-d ₆	2.1-2.6 1.6-2.1	8.2	8.1 (9,2)		7.3-8.0		
1a n = 5	DMSO-d ₆	2.1-2.7 1.4-1.8	8.5	8.5 (8,2)		7.6-8.2		
1b n = 4	CDCl ₃	2.3-2.8 1.8-2.2	7.9	8.3 (8,2)		7.2-7.9		3.7 (3H, s)
1b n = 5	CDCl ₃	2.2-2.6 1.5-1.8	7.8	8.3 (8,2)		7.2-7.7		3.7 (3H, s)
2a n = 4	CDCl ₃	2.5-3.0 1.8-2.3	2.6	8.8 (9,2)		7.8-8.3		
2a n = 5	DMSO-d ₆	2.1-2.7 1.3-1.8	2.4	8.1 (8,2)		7.3-7.8		
2b n = 4	CCl ₄	2.2-2.7 1.5-2.1	2.4	8.2 (8,2)		7.3-7.9		3.7 (3H, s)
2b n = 5	CCl ₄	2.1-2.7 1.3-1.8	2.4	8.7 (8,2)		7.5-8.3		3.6 (3H, s)
3a n = 3	DMSO-d ₆	2.7 ----	8.5	8.4 (8)	7.3 (8,2)	---	7.2 (2)	
3a n = 4	DMSO-d ₆	2.1-2.4 1.5-2.0	8.0	7.9 (8)	6.9 (8,2)	---	6.8 (2)	
3a n = 5	DMSO-d ₆	2.2-2.9 1.5-1.9	8.7	8.5 (9)	7.5 (9,2)	---	7.4 (2)	
3a n = 6	DMSO-d ₆	2.1-2.8 1.2-1.8	8.1	8.0 (9)	7.0 (9,2)	---	6.9 (2)	
3b n = 3	DMSO-d ₆	2.6 ----	8.1	8.0 (7)	6.9 (7,2)	---	6.9 (2)	1.2 (3H, t), 4.1 (2H, q)
3b n = 4	CDCl ₄	2.3-2.8 1.9-2.3	8.0	8.4 (9)	7.3 (9,2)	---	7.1 (2)	1.3 (3H, t), 4.2 (2H, q)
3b n = 5	DMSO-d ₆	2.3-2.8 1.4-1.8	8.5	8.4 (9)	7.3 (9,2)	---	7.2 (2)	1.2 (3H, t), 4.3 (2H, q)
3b n = 6	CCl ₄	2.5-3.1 1.6-2.2	8.5	9.5 (10)	8.2 (10,2)	9.0	8.1 (2)	1.4 (3H, t), 4.8 (2H, q)
4a n = 3	DMSO-d ₆	2.8 ----	8.6	8.4 (10)	7.5 (10,2)	4.1	7.5 (2)	
4a n = 4	DMSO-d ₆	2.1-2.6 1.6-2.0	8.1	8.0 (9)	7.0 (9,2)	3.9	7.1 (2)	
4a n = 5	DMSO-d ₆	2.0-2.5 1.4-1.7	8.1	8.0 (9)	7.0 (9,2)	3.9	7.1 (2)	
4a n = 6	CDCl ₃	2.2-2.7 1.4-1.9	7.8	8.2 (10)	7.1 (10,2)	3.9	6.8 (2)	
4b n = 3	CDCl ₃	3.0 ----	8.2	8.5 (7)	7.4 (7,2)	4.2	7.3 (2)	1.4 (3H, t), 4.5 (2H, q)
4b n = 4	CDCl ₃	2.3-2.8 1.9-2.2	8.0	8.4 (9)	7.1 (9,2)	4.0	7.0 (2)	1.3 (3H, t), 4.2 (2H, q)
4b n = 5	CDCl ₃	2.4-2.9 1.7-2.0	8.6	9.0 (9)	7.8 (9,2)	4.3	7.6 (2)	1.4 (3H, t), 4.6 (2H, q)
4b n = 6	CDCl ₃	2.2-2.6 1.3-1.9	7.4	7.8 (9)	6.7 (9,2)	3.8	6.6 (2)	1.3 (3H, t), 4.0 (2H, q)
5a n = 2	DMSO-d ₆	3.4 ----	2.4	7.9 (9)	6.9 (9,2)	---	6.8 (2)	
5a n = 3	DMSO-d ₆	2.2-2.8 ----	2.4	7.8 (9)	6.8 (9,2)	---	6.7 (2)	
5a n = 4	DMSO-d ₆	2.2-2.7 1.5-2.0	2.4	7.0 (9)	7.1 (9,2)	---	6.9 (2)	
5a n = 5	DMSO-d ₆	2.1-2.7 1.3-1.8	2.5	8.1 (9)	7.1 (9,2)	---	6.9 (2)	
5a n = 6	DMSO-d ₆	2.1-2.8 1.2-1.8	2.5	8.5 (9)	7.4 (9,2)	---	7.3 (2)	
5b n = 5	CDCl ₃	2.2-2.8 1.5-2.1	2.5	8.2 (9)	7.2 (9,2)	10.1	7.1 (2)	1.3 (3H, t), 4.2 (2H, q)
6 n = 2	CDCl ₃	3.5 ----	2.4	8.1 (9)	7.0 (9,2)	2.3	7.2 (2)	1.3 (3H, t), 4.1 (2H, q)
6 n = 3	CDCl ₃	2.3-3.0 ----	2.5	8.2 (8)	7.1 (8,2)	2.3	7.2 (2)	1.2 (3H, t), 4.1 (2H, q)
6 n = 4	CCl ₄	2.2-2.7 1.6-2.0	2.4	8.2 (8)	7.1 (8,2)	2.1	7.2 (2)	1.3 (3H, t), 4.1 (2H, q)
6 n = 5	CCl ₄	2.1-2.6 1.3-1.8	2.3	8.0 (8)	6.9 (8,2)	2.2	7.1 (2)	1.2 (3H, t), 4.0 (2H, q)
6 n = 6	CCl ₄	2.3-2.9 1.4-2.0	2.6	8.8 (9)	7.6 (9,2)	2.5	7.7 (2)	1.3 (3H, t), 4.4 (2H, q)

Table 4
Preparation and Some Physical data of ω -Benzoylalkanoates 7b and 8b

	Yield	Bp/°C	Mp/°C	IR/cm ⁻¹	M ⁺ (m/z)
7b n = 4	58%	154-156 (2 mm Hg)	39-40	1730, 1645	236
7b n = 5	32%	182-184 (3 mm Hg)	37.5-38.5	1740, 1645	250
8b n = 2	69%	193-195 (3 mm Hg)	---	3400, 1705	238
8b n = 3	55%	200-212 (3 mm Hg)	56-57 [a]	3300, 1695	252
8b n = 4	59%	227-240 (4 mm Hg)	56.5-58 [a]	3300, 1700	266
8b n = 5	54%	220-230 (3 mm Hg)	56.5-57.5 [a]	3350, 1700	280
8b n = 6	47%	234-235 (4 mm Hg)	64-65 [a]	3300, 1705	294

[a] After recrystallization from benzene-cyclohexane.



ω -(7-acetoxy-2-methyl-3-chromonyl)alkanoates **b**, $n = 2-6$. Cyclization of **8b**, $n = 2$ with *N,N*-dimethylformamide dimethyl acetal gave a complex mixture, because the active methylene formed in the products might cause further reactions. These results are also summarized in Table 1. Hydrolysis of ω -(3-chromonyl)alkanoates **1b** and **2b**, $n = 4, 5$, **3b** and **4b**, $n = 3-6$, **5b**, $n = 5, 6$, $n = 2-6$, thus obtained, gave corresponding acids **1a** and **2a**, $n = 4, 5$, **3a** and **4a**, $n = 3-6$, **5a**, $n = 2-6$ effectively after refluxing in 20% aqueous sulfuric acid [2].

EXPERIMENTAL

All melting points were measured on a micro melting point apparatus (Yanagimoto), and they are uncorrected. The ir spectra were taken on a Hitachi EPI-S2 spectrophotometer as liquid films or potassium bromide disks. Mass spectra were recorded on a JEOL JMS-OISG-2 spectrometer. Some physical data, elemental analyses of the new chromones are summarized in Table 2. The pmr spectra were recorded on a JEOL JNM-MH-60 or JEOL PMX-60Si spectrometer, and the data of new chromones are listed in Table 3.

Preparation of Keto Acids **7a**, **8a** by Acylation of the Enamine.

According to the procedure reported by Hall and Plant [1], 5-(2-hydroxybenzoyl)pentanoic acid **7a**, $n = 4$, 6-(2-hydroxybenzoyl)hexanoic acid **7a**, $n = 5$, and 6-(2,4-dihydroxybenzoyl)hexanoic acid **8a**, $n = 5$ were prepared by acylation of the enamines, 1-pyrrolidinocyclopentene or 1-pyrrolidinocyclohexenes, with 2-acetoxybenzoyl chloride or 2,4-diacetoxybenzoyl chloride followed by alkaline cleavage of the intermediate, 9*H*-cyclopenteno[*b*]chromen-9-one, 1,2,3,4-tetrahydroxanthone, or 6-hydroxy-1,2,3,4-tetrahydroxanthone, with potassium hydroxide aqueous solution.

Keto Acids **8b**, $n = 2-6$ from Resorcinol.

According to the procedure reported by Desai and Figueredo [3], ω -(2,4-Dihydroxybenzoyl)alkanoic acids, **8a**, $n = 2, 3$ were prepared from resorcinol and succinic anhydride $n = 2$ or glutaric anhydride $n = 3$. Similarly, other ω -(2,4-dihydroxybenzoyl)alkanoic acids, **8a**, $n = 4-6$ were prepared from resorcinol and ω -ethoxycarbonylalkanoyl chloride.

Conversion of Keto Acids **7a** and **8a** to their Esters **7b** and **8b**.

Two ω -(2-hydroxybenzoyl)alkanoic acids **7a**, $n = 4, 5$ were converted to their methyl esters **7b**, $n = 4, 5$ by refluxing in methanol with a catalytic amount of sulfuric acid. The other five ω -(2,4-dihydroxybenzoyl)alkanoic acids **8a**, $n = 2-6$ were converted to their ethyl esters **8b**, $n = 2-6$ by a similar esterification in ethanol. These results are summarized in Table 4.

Cyclization of **7b**, $n = 4, 5$ with Ethyl Formate-Sodium Metal.

To powdered sodium metal (1.15 g, 50 mmoles) was slowly added a mixture of ethyl formate (100 mmoles) and ω -(2-hydroxybenzoyl)alkanoate **7b** (10 mmoles) with stirring and allowed to stand overnight. After treatment of the excess sodium metal with methanol, the reaction mixture was acidified with 10% hydrochloric acid and was heated on a water bath for 15 minutes. After cooling, the mixture was extracted with ether. The ether layer was washed with saturated sodium hydrogencarbonate aqueous solution, and then with saturated sodium chloride aqueous solution, and dried over anhydrous sodium sulfate. After removal of the solvent, the residual oil was purified by a silica-gel column. The fractions eluted by benzene-chloroform (7:3) gave ω -(3-chromonyl)alkanoates **1b**, $n = 4, 5$. The sodium hydrogencarbonate layer was acidified with 10% hydrochloric acid, and the resulting precipitate was recrystallized from benzene to give ω -(3-chromonyl)alkanoic acids **1a**, $n = 4, 5$. These acids were also prepared in 53% ($n = 4$), 58% ($n = 5$) yield after refluxing in 20% aqueous sulfuric acid for 5 hours.

Cyclization of **7b**, $n = 4, 5$ with Acetic Anhydride-Sodium Acetate.

A mixture of methyl ω -(2-hydroxybenzoyl)alkanoate, **7b**, $n = 4, 5$ (4.40 mmoles), acetic anhydride (8.80 mmoles), and anhydrous sodium acetate (8.80 mmoles) was refluxed for 4 hours. After treatment of ice-water, the mixture was extracted with chloroform. The chloroform layer was washed with 10% hydrochloric acid, 5% sodium hydroxide aqueous solution, and saturated sodium chloride aqueous solution, and then dried over anhydrous sodium sulfate. After removal of the solvent, the oily residue was purified by a silica-gel column. The fractions eluted by chloroform was recrystallized from hexane to give methyl ω -(2-methyl-3-chromonyl)alkanoates **2b**, $n = 4, 5$. The precipitate obtained by acidification of the sodium hydroxide layer was recrystallized from benzene-ethanol to give ω -(7-hydroxy-3-chromonyl)alkanoic acids **2a**, $n = 4, 5$. The acid **2a**, $n = 4$ was also obtained in 33% yield after hydrolysis in 20% aqueous sulfuric acid.

Cyclization of **8b**, $n = 2-6$ with *N,N*-Dimethylformamide Dimethyl Acetal.

A mixture of ethyl ω -(7-hydroxy-3-chromonyl)alkanoate **8b** and *N,N*-dimethylformamide dimethyl acetal (2.5 molar equivalents) was heated in dry xylene at 120° for 2 hours, and then at 150-160° for 30 minutes thus removing the generated methanol. After removal of the solvent, the residual oil was chromatogrammed on a silica gel column. The fractions eluted with benzene-chloroform (2:8) were crystallized from cyclohexane to give ethyl ω -(7-methoxy-3-chromonyl)alkanoate **4b**. The fraction eluted by chloroform-ethanol (1:1) was recrystallized from benzene to give methyl ω -(7-hydroxy-3-chromonyl)alkanoate **3b**. These esters, **3b** and **4b**, $n = 3-6$ were converted to the corresponding acids **3a** and **4a**, $n = 3-6$ after refluxing in 20% aqueous sulfuric acid. The yields were 41%, **3a**, $n = 3$, 31%, **3a**, $n = 4$, 52%, **3a**, $n = 5$, 45%, **3a**, $n = 6$, 42%, **4a**, $n = 3$, 24%, **4a**, $n = 4$, 34%, **4a**, $n = 5$, and 53%, **4a**, $n = 6$.

Cyclization of **8b**, $n = 2-6$ with Acetic Anhydride-DBU.

A mixture of ethyl ω -(2,4-dihydroxybenzoyl)alkanoate, **8b**, $n = 2-6$ (4.00 mmoles), acetic anhydride (12.0 mmoles), and DBU

(1,8-diazabicyclo[5.4.0]-7-undecene) (3.20 mmoles) was refluxed for 4 hours, and treated similarly. The neutral oily products eluted with chloroform were crystallized from hexane to give ethyl ω -(7-acetoxy-3-chromonyl)alkanoates **6**, $n = 2-6$, and ethyl ω -(7-hydroxy-3-chromonyl)pentanoate, **5b**, $n = 5$ also obtained as the fractions eluted by ethanol:chloroform (1:99). The acidic precipitate was recrystallized from benzene-ethanol to give ω -(7-hydroxy-3-chromonyl)alkanoic acids **5a**, $n = 2-4, 6$. these results are summarized in Table 1. The esters **5b**, $n = 5$, **6**, $n = 2-6$ were also converted to the corresponding acids, **5a**, $n = 2-6$

in 86%, $n = 2$, 90%, $n = 3$, 29%, $n = 4$, 64%, $n = 5$, from **6**, 66%, $n = 5$, from **5b**, 38%, $n = 6$, yield after refluxing in 20% aqueous sulfuric acid for 5 hours.

REFERENCES AND NOTES

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