269. ^{13}C-NMR. Spectral Differences between Corresponding Methyl Esters, Phenyl Esters and 2-Substituted Chromones

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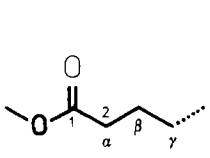
Summary

The ^{13}C-NMR. spectra of 2-substituted chromones (**3**) are compared with the data of the analogous methyl and phenyl esters (**1** and **2**). The chemical shift differences found are most prominent for the C-atoms in β-position to the ester carbonyl and chromone C(2), respectively. These shift differences are discussed in terms of conformational differences between the esters **1** and **2** and the analogous chromones **3**.

During an investigation of the relative configurations in the bioxirane part of the antibiotic hedamycin [1] we noticed, that methyl esters **1** can well serve as model compounds for 2-substituted chromones **3** in ^{13}C-NMR studies. However, the C-atoms in β-position to the carbonyl group in the methyl esters **1j** and **1k** absorbed *ca.* 3 ppm at higher field than the corresponding C-atoms in the chromone **3j** and in hedamycin, respectively.

We present here a ^{13}C-NMR. spectral comparison of a series of structurally related methyl esters **1**, phenyl esters **2** and 2-substituted chromones **3** (see *Scheme*).



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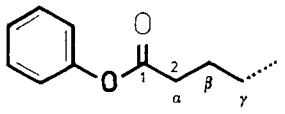

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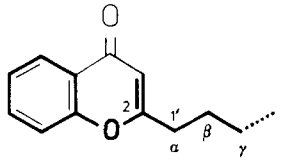

3

The methyl and phenyl esters were mostly known compounds which were commercially available or synthesized along standard routes. Most of the 2-substituted chromones presented here were prepared using *Koo*'s procedure [2]: 0-hydroxyacetophenone (**4**) was condensed with the appropriate methyl ester **1b–f** in the presence of sodium hydride. For the synthesis of **5b** ethyl acetate and sodium were preferred [3]. The 1,3-diketones **5b–f** so obtained were cyclized with conc. hydrochloric acid to give the chromones **3b–f**. The chromones with olefinic substituents were epoxidized with *m*-chloroperbenzoic acid in refluxing dichloromethane.

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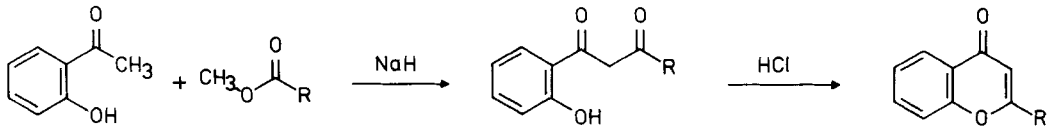


4 **1b-f** **5b-f** **3b-f**

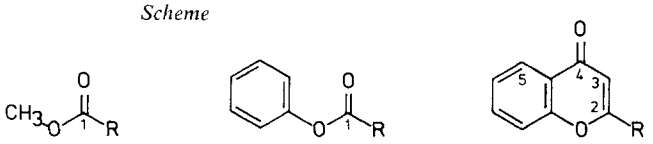
R: see *Scheme*, p. 2656

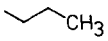
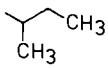
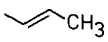
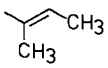
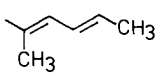
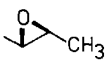
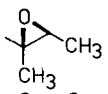
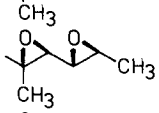
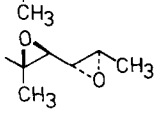
The ^{13}C-NMR. chemical shifts are compiled in the *Table*. The compounds were mostly measured in *ca.* 2M solutions in $CDCl_3$. Two spectra each were measured at different concentrations for compounds **1d** (3.7M, 5M), **3d** (2M, 3M) and **3j** (0.5M, 1.5M). The chemical shift differences from these concentration changes were smaller the ± 0.1 ppm for all sp^3- and most sp^2-C-atoms and thus within the experimental error for routine ^{13}C-NMR. spectra. The assignments of the ^{13}C-resonances were in general straightforward from the multiplicities (off-resonance decoupled spectra were run for all compounds) and from comparison with related substances [4]. The spectrum of the unsubstituted chromone (**3a**) was used for the assignments of the sp^2-C-resonances in the chromone series. The two oxirane C-resonances in the spectra of **2i** and **3i** could be distinguished from their coupling patterns, which were compared with those of the methyl ester **1i** [5]. Thus, in the spectrum of the phenyl ester **2i** the resonance at 53.8 ppm showing $^1J(C,H) = 185.7$ Hz, $^2J(C,H) = 1.7$ Hz and $^3J(C,H) = 4.6$ Hz was assigned to C(2); the signal at 54.8 ppm with $^1J(C,H) = 178.0$ Hz, $^2J(C,H) = 5.6$ Hz (with CH_3) and $^2J(C,H) = 2.5$ Hz then belongs to C(3). In the spectrum of the chromone **3i** the values for the α-C-atom C(1′) (55.5 ppm) are: $^1J(C,H) = 180.7$ Hz, $^2J(C,H) = \sim 2$ Hz, $^3J(C,H) = \sim 5$ Hz and $^3J(C,H) = \sim 4$ Hz (with H–C(3)), and for the β-C-atom C(2′) (57.0 ppm): $^1J(C,H) = 176.9$ Hz, $^2J(C,H) = 5.4$ Hz (with CH_3) and $^2J(C,H) = 2.4$ Hz. The distinction of the methyl group signals in **2j** and **3j** was also possible by comparison of their splitting patterns with those described for the corresponding methyl ester **1j** [5]. The resonances at 13.3 ppm in the spectrum of the phenyl ester **2j** and at 14.0 ppm in that of the chromone **3j** showed no two- or three-bond couplings. This clearly identifies them as the signals of the C(α)-methyl groups. The other two methyl resonances exhibit the expected two-bond splitting (**2j**: 6.1 Hz for the signal at 13.4 ppm; **3j** 6.8 Hz for the line at 13.9 ppm).

The data compiled in the table show that in general the chemical shifts of the C-atoms of the R groups are not very sensitive to the change from methyl esters to phenyl esters or to chromones. The most prominent shift differences can be seen at C(β). This C-atom, as well as CH_3–C(α), is three bonds away from the position where the structural differences between esters and chromones are most important, *viz.* the carbonyl O-atom and the chromone CH-group, respectively. This suggests that the chemical shift differences observed for C(β) and for CH_3–C(α) are mainly due to steric effects ("γ-effect"). However, space-filling molecular models (CPK) of the three skeletons **1**, **2** and **3** do not reveal any important differences in steric relationships; the spatial requirements of the carbonyl O-atom corresponds more or less to that of the chromone CH-group. On the other hand, the magnetic anisotropy of a

carbonyl group is different from that of a C,C-double bond. And again C(β) and CH_3–C(α) are those atoms, which will "feel" most prominently such differences upon conformational changes along the bond attaching the R group to the ester carbonyl or the chromone ring.

Scheme



R =				
	H			**3a**
	CH_3	**1b**	**2b**	**3b**
		**1c**	**2c**	**3c**
		**1d**	**2d**	**3d**
		**1e**	**2e**	**3e**
		**1f**	**2f**	**3f**
		**1g**		**3g**
		**1h**	**2h**	**3h**
		**1i**	**2i**	**3i**
		**1j**	**2j**	**3j**
		**1k**		**3k**
		**1l**		**3l**

In the compounds with unsaturated R groups (series **e–h**) replacement of the methyl ester by the phenyl ester induces a 2 ppm downfield shift in C(β), which might be explained as a consequence of an intensification of the carbonyl group polarization by the phenoxy group. This is confirmed by the downfield shift of *ca.* 0.2 ppm observed for the C(β) protons in **2e** and **2f** with respect to **1e** and **1f**. However, the

Table. *^{13}C-NMR. data of the methyl esters* **1**, *phenyl esters* **2** *and chromones* **3**[a])

	C(α)	H_3C–C(α)	C(β)	C(γ)	C(δ)	C(ε)	Other C-atoms[b])
Compounds with saturated R							
3a							155.6, 112.8, 177.1, 124.9, 125,5*, 125.1*, 133.7, 118.2, 156.4
1b	20.6						171.3, 51.5
2b	20.9						169.3, 150.5, 121.6, 129.4, 125.8
3b	20.4						166.0, 110.6, 177.9, 123.7, 125.6*, 124.9*, 133.3, 117.8, 156.5
1c	36.1		18.6	13.7			173.9, 51.3
2c	36.3		18.5	13.6			171.8, 151.0, 121.6, 129.4, 125.6
3c	36.2		20.2	13.5			169.4, 109.8, 177.9, 123.8, 125.6*, 124.8*, 133.3, 117.9, 156.5
1d	41.3	16.8	27.3	11.7			176.5, 51.2
2d	41.2	16.5	26.9	11.6			174.8, 151.1, 121.2, 129.3, 125.6
3d	40.4	17.8	27.5	11.6			173.0, 108.8, 177.9, 123.9, 125.5*, 124.8*, 133.3, 117.9, 156.5
Compounds with unsaturated R							
1e	122.8		144.6	17.8			[5]
2e	122.3		146.6	18.0			164.6, 151.0, 121.7, 129.3, 125.6
3e	124.3*		136.3	18.5			161.7, 109.0, 178.4, 124.1, 125.6*, 124.8*, 133.5, 117.8, 156.0
1f	128.9	12.0	136.9	14.2			[5]
2f	128.4	12.1	139.0	14.5			166.3, 151.4, 121.8, 129.3, 125.4
3f	128.1	12.0	131.1	14.4			164.1, 106.8, 178.3, 123.7, 125.3*, 124.6*, 133.4, 117.8, 155.9
1g	124.9	12.5	138.8	127.7	137.5	18.8	[10]
3g	124.5	12.6	133.4	127.5	137.3	18.9	164.1, 107.2, 178.1, 123.7, 125.3*, 124.6*, 133.4, 117.7, 155.8
1h	130.5		129.7	128.4	132.9		167.0, 51.9
2h	129.7		130.1	128.5	133.4		164.5, 151.1, 121.7, 129.4, 125.8
3h	131.8		126.2	128.9	131.4		163.2, 107.5, 178.0, 124.0, 125.6*, 125.1*, 133.6, 118.0, 156.2
Compounds with epoxy-R							
1i	53.8		54.4	17.1			[5]
2i	53.8		54.8	17.0			167.6, 150.4, 121.3, 129.5, 126.1
3i	55.5		57.0	17.4			164.1, 109.1, 177.5, 124.3, 125.8*, 125.3*, 133.8, 117.9, 156.3
1j	57.3	13.3	57.8	13.4			[5]
2j	57.4	13.3	58.1	13.4			170.0, 150.7, 121.3, 129.4, 126.0
3j	57.6	14.0	61.3	13.9			168.3, 107.3, 178.1, 124.0, 125.8*, 125.3*, 133.7, 118.0, 156.3
1k	57.2	14.0	60.8	55.4	51.5	17.1	[1]
3k	57.6	14.7	63.6	55.4	51.5	17.1	[6]
1l	57.4	13.7	60.5	55.0	53.6	17.1	[1]
3l	57.8	14.5	63.1	55.2	53.5	17.0	[6]

a) Chemical shifts given in ppm downfield from internal TMS. Assignments with asterisks my be interchanged.

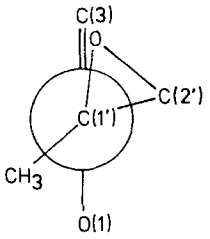
b) Given in the following order: for methyl esters: carbonyl, methoxy; for phenyl esters: carbonyl, *ipso, o, m, p;* for chromones: C-atoms no. 2, 3, 4, 4a, 5, 6, 7, 8, 8a.

large (5–8 ppm) upfield shift experienced by C(β) upon replacement of the methyl ester by the chromone skeleton can hardly be interpreted in terms of mesomery, since the chemical shifts of C(γ) and C(δ) in **3g** are roughly the same as in **1g**. In addition, *all* the proton resonances of the diene chain of **3g** including the methyl groups are slightly shifted *down*field (0.06–0.16 ppm) when compared with **1g**. The observed upfield shift of C(β) must therefore be due to a steric effect caused by the chromone H–C(3) in a conformation where the aromatic nucleus and the olefinic

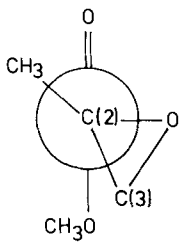
substituent are coplanar. The phenyl residue of flavone (**3h**) cannot be compared so well with the other unsaturated R groups. However, it is noteworthy, that it follows the abovementioned shift trends, but the effects are not so pronounced.

In the series of compounds with saturated hydrocarbon R groups (**b–d**) prominent shift differences are again noted only for C-atoms three bonds away from the carbonyl O-atom and the chromone CH-group, respectively. The C(β)resonance of **3c** is shifted downfield 1.6 ppm with respect to **1c**, whereas in **3d** this C-atom is unaffected, but CH_3–C(α) is shifted 1.0 ppm downfield. These data can be interpreted in terms of different torsion at angles about the C(1)–C(2) bond in the esters, and about the C(2)–C(1′) bond in the chromones. These differences are not the same for series **c** and **d** due to the presence of the extra methyl group in the compounds **d**.

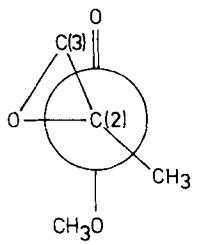
In the series with an epoxy R group (**i–l**), the chromone **3i** exhibits a peculiarity: its C(α) resonance is shifted 1.7 ppm downfield with respect to **1i**; we cannot explain this; yet the compounds **i** have no CH_3–C(α). The C(β) signals of the series **i–l** show a consistent downfield shift of *ca.* 3 ppm upon replacement of the ester group by the chromone; the methyl groups at C(α) experience a smaller downfield shift (0.7 ppm). Again, we think that this is due to a conformational change when going from the esters **1** or **2** to the chromones **3**. While we do not know the exact conformation of the esters, the solid state conformation of the chromone **3l** was recently determined [6]. In this conformation the two C,O-dipoles are antiperiplanar as shown in the *Newman* projection **A** (along the C(1′), C(2)-bond) below. In the ester series where H–C(3) of the chromone is replaced by the carbonyl O-atom, conformation **B** or **C** might be favored to minimize dipole-dipole interactions. Such a change of conformation and the change of the magnetically anisotropic environment (C=O *vs.* C=C) that go along with the change from the esters to the 2-substituted chromones must be responsible for the downfield shifts observed for the β-C-atom C(2′) and CH_3–C(α).



A



B



C

The conformations of the compounds studied seem to be governed by three different principles according to the nature of R: least steric hindrance in the series with saturated hydrocarbon R, coplanarity (leading to interaction with the chromone CH) in the olefinic compounds and dipole-dipole repulsion in the epoxy series.

This work was supported by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung*, which is gratefully acknowledged.

Experimental Part

1. General remarks. – Melting points were determined on a *Kofler* hot stage and are corrected; error *ca.* ±2°. The spectra were measured in the spectral laboratory of the Institute (the skillful aid of *K. Aegerter* is gratefully acknowledged) on the following instruments: UV.: *Beckman DK 2, Beckman 25, Cary 219;* IR.: *Perkin-Elmer 125,* ^{1}H-NMR.: *Varian A-60* (60 MHz), *Varian EM 360* (60 MHz), *Varian EM 390* (90 MHz) or *Bruker WH 90* (90 MHz FT); ^{13}C-NMR.: *Bruker WH 90* (22.63 MHz FT). Microanalyses were carried out by *E. Thommen* of our Institute. Abbreviations: i. V. = *in vacuo*, RT. = room temperature, TLC. = thin layer chromatography.

2. Methyl esters. – 2.1. *Methyl acetate* (**1b**). Commercial *(Fluka AG)*; ^{13}C-NMR. (22.63 MHz, 2.0M in $CDCl_3$): see *Table* (*cf.* [4], no. 3205).

2.2. *Methyl butyrate* (**1c**). Commercial *(Fluka AG);* ^{13}C-NMR. (22.63 MHz, 2.5M in $CDCl_3$): see *Table* (*cf.* [4], no. 6054).

2.3. *Methyl 2-methylbutyrate* (**1d**). 2-Methylbutyric acid (100 ml, 0.91 mol, a gift of *BASF*, Ludwigshafen) was dissolved in methanol (500 ml, 12.34 mol). After the addition of conc. sulfuric acid (25 ml) the mixture was left at RT. for 1 d, after which it was refluxed for 6 h. Then half-saturated aqueous NaCl-solution (500 ml) was added, whereupon the crude ester separated. The mixture was extracted with three 150 ml portions of CH_2Cl_2 which were washed twice with 150 ml of sat. aqueous $KHCO_3$-solution. The combined CH_2Cl_2 portions were dried with $MgSO_4$, filtered and evaporated. The crude ester was distilled and the fraction boiling at 114–115°/*ca.* 1 bar ([7]: 114.4–115.4°/*ca.* 1 bar) gave 79,4 g (74.8%) of pure **1d** which, according to its ^{13}C-NMR. spectrum, was free of methyl isovaleriate. – ^{1}H-NMR (60 MHz, $CDCl_3$): 3.64 (*s*, 3 H, OCH_3); 2.37 (*sextet*, J=6.6, 1 H, CH); 2.0–1.3 (*m*, 2 H, CH_2); 1.13 (*d*, J=6.6, 3 H, CH_3); 0.90 (*t*, J=6.6, 3 H, CH_3). – ^{13}C-NMR. (22.63 MHz, 5.2M in $CDCl_3$): see *Table* (*cf.* [8]).

2.3. *Methyl crotonate* (**1e**). Commercial *(Fluka AG).* – ^{13}C-NMR. (22.63 MHz, 5.0M in $CDCl_3$): see *Table* (from [5]).

2.4. *Methyl 2-methylcrotonate* (**1f**). 2-Methylcrotonic acid (50 g, 0,5 mol, *purum, Fluka AG*) was esterified as described in *Chapt. 2.3.* The crude ester was distilled i. V. and 42.1 g (73.8%) of pure **1f** were collected at 48°/31 mbar ([9]: 137.5–138.8°/1009 mbar). – ^{13}C-NMR. (22.63 MHz, 5.0M in $CDCl_3$): see *Table* (from [5]).

2.5. *Methyl (2*E*,4*E*)-2-methyl-2,4-hexadienoate* (**1g**). See [10]. – ^{13}C-NMR. (22.63 MHz, 3.5M in $CDCl_3$): see *Table* (from [10]).

2.6. *Methyl benzoate* (**1h**). Commercial *(Fluka AG).* – ^{13}C-NMR. (22.63 MHz, 1.8M in $CDCl_3$): see *Table* (*cf.* [4], no. 695).

2.7. *Methyl (2*R*,*3*S**)-2,3-epoxybutyrate* (**1i**). See [5]. – ^{13}C-NMR. (22.63 MHz, 4.6M in $CDCl_3$): see *Table* (from [5]).

2.8. *Methyl (2*R*,*3*S**)-2,3-epoxy-2-methylbutyrate* (**1j**). See [5]. – ^{13}C-NMR. (22.63 MHz, 5.0M in $CDCl_3$): see *Table* (from [5]).

2.9. *Methyl (2*R*,*3*S*,*4*R*,*5*S**)-2,3:4,5-diepoxy-2-methylhexanoate* (**1k**). See [10]. – ^{13}C-NMR. (22.63 MHz, 0.6M in $CDCl_3$): see *Table* (from [1]).

2.10. *Methyl (2*R*,*3*S*,*4*S*,*5*R**)-2,3:4,5-diepoxy-2-methylhexanoate* (**1l**). See [10]. – ^{13}C-NMR. (22.63 MHz, *ca.* 2M in $CDCl_3$): see *Table* (from [1]).

3. Phenyl esters. – 3.1. *Phenyl acetate* (**2b**). Commercial *(Fluka AG).* – ^{13}C-NMR. (22.63 MHz, *ca.* 4M in $CDCl_3$): see *Table* (*cf.* [4], no. 1207).

3.2. *Phenyl butyrate* (**2c**). To 9.41 g (0.1 mol) of phenol was added 10.65 g (0.1 mol) of butyryl chloride *(Fluka AG).* The mixture was gently refluxed on a steam bath until the evolution of HCl subsided (2h). The almost colorless crude product was then distilled i. V. The fraction 105–107°/17.3 mbar ([11]; 143°/27 mbar) was collected. Yield 13.22 g (80%). – ^{1}H-NMR. (90 MHz, $CDCl_3$): 7.5–7.0 (*m*, 5 H, arom. H); 2.50 (*t*, J=7, 2 H, CH_2); 1.74 (*sextet*, J=7, 2 H, CH_2); 0.98 (*t*, J=7, 3 H, CH_3). – ^{13}C-NMR. (22.63 MHz, 2.2M in $CDCl_3$): see *Table.*

3.3. Phenyl 2-methylbutyrate (**2d**). 2-Methylbutyric acid (10.21 g, 0.1 mol, a gift of *BASF*, Ludwigshafen) was heated together with thionyl chloride (11.9 g, 0.1 mol) on a steam bath for 1 h. Then, phenol (9.41 g, 0.1 mol) was added and the mixture heated for an additional hour. The brown reaction product was allowed to cool and was then distilled under diminished pressure. The distillate (16.69 g) was taken up in 100 ml of CH_2Cl_2, which was then extracted successively with 70 ml of ice cold 2N NaOH and 70 ml of ice water. The aqueous portions were washed with 100 ml of CH_2Cl_2. The organic layers were combined, dried over $MgSO_4$ and filtered. Removal of the solvent yielded 13.92 g of **2d** as a slightly yel-

low oil. Distillation i. V. gave 12.66 g (71.1%) of pure ester boiling at 111–112°/17.3 mbar. – UV. (ethanol): 208 (4200), 252 *S* (210), 258 (240), 265 (180). – IR (film): 2975, 2940, 2880, 1760, 1595, 1495, 1460, 1200, 1165, 1125, 750, 690. – ^{1}H-NMR. (90 MHz, $CDCl_3$): 7.5–7.0 (*m*, 5 H, arom. H); 2.62 (*sextet*, J=7, 1 H, CH); 2.1–1.4 (*m*, 2 H, CH_2); 1.28 (*d*, J=7, 3 H, CH_3); 1.03 (*t*, J=7.5, 3 H, CH_3). – ^{13}C-NMR. (22.63 MHz, 2.0M in $CDCl_3$): see *Table*.

$C_{11}H_{14}O_2$ (178.23) Calc. C 74.13 H 7.92% Found C 74.23 H 8.12%

3.4. *Phenyl crotonate* (**2e**). Crotonic acid (8.7 g, 0.1 mol, *Fluka AG*), phenol (9.5 g, 0.1 mol) and conc. sulfuric acid (0.3 ml) were dissolved in 150 ml of toluene. The mixture was then refluxed for 24 h using a *Dean & Stark* apparatus (which was cooled in an ice bath) and was then allowed to cool [12]. The toluene phase was extracted successively with 100 ml of ice-cold 2N NaOH and 100 ml of ice-cold water. The organic layer was dried over $MgSO_4$, filtered and evaporated to give 10.06 g of a yellowish oil. Distillation i. V. gave pure **2e**, b. p. 119–120°/17 mbar ([13]: 115–118°/16 mbar). Yield 7.96 g (49%). – ^{1}H-NMR. (90 MHz, $CDCl_3$): 7.5–6.9 (*m*, 6 H, arom. H, vinyl. H); 6.03 (*d* × *qa*, J=16 and 2, 1 H, vinyl. H); 1.90 (*d* × *d*, J=7 and 2, 3 H, CH_3). A small signal at 2.18 (*d* × *d*, J=7 and 2) indicated that the product contained *ca.* 2.5% of isocrotonate. – ^{13}C-NMR. (22.63 MHz, 1.8M in $CDCl_3$): see *Table*.

$C_{10}H_{10}O_2$ (162.19) Calc. C 74.05 H 6.22% Found C 73.97 H 6.37%

3.5. *Phenyl 2-methylcrotonate* (**2f**). 2-Methylcrotonic acid (10.0 g, 0,1 mol, *Fluka AG*), phenol (9.4 g, 0.1 mol) and conc. sulfuric acid (0.3 ml) were esterified and worked up as deresited in 3.4. After extraction with 2N NaOH and ice-cold water the aqueous phases were washed with 70 ml of toluene. The organic layers were combined, dried over $MgSO_4$ and evaporated. A yellowish oil resulted (10.55 g), which was distilled i.V. to yield 8.23 g (46.7%) of almost pure **2f**, b. p. 128–130°/17 mbar. An analytically pure sample was obtained by redistillation, b. p. 131°/19 mbar ([13]: 124–126°/16 mbar). – ^{1}H-NMR. (90 MHz, $CDCl_3$): 7.5–6.9 (*m*, 6 H, arom. H, vinyl. H); 1.90 (*qa*, J=1.5, 3 H, CH_3); 1.78 (*d* × *qa*, J=7 and 1.5, 3 H, CH_3). – ^{13}C-NMR. (22.63 MHz, 2.2M in $CDCl_3$): see *Table*.

$C_{11}H_{12}O_2$ (176.22) Calc. C 74.97 H 6.86% Found C 74.72 H 6.71%

3.6. *Phenyl benzoate* (**2h**). Commercial *(Fluka AG)*. – ^{13}C-NMR. (22.63 MHz, 2.1M in $CDCl_3$): see *Table* (*cf.* [4] no. 7290).

3.7. *Phenyl (2*R*,3*S*)-2,3-epoxybutyrate* (**2i**). Phenyl crotonate (**2e**, 4 g, 24.7 mmol) was dissolved in a solution of *m*-chloroperbenzoic acid (6.38 g, 90%, 37 mmol) in 150 ml of CH_2Cl_2. The solution was refluxed for 14 d. ^{1}H-NMR. spectroscopy showed 77% epoxidation. After cooling and filtration, the solution was extracted successively with 200 ml of 10% Na_2SO_3-solution and 200 ml of 5% $NaHCO_3$-solution. The aqueous phases were washed with 150 ml of CH_2Cl_2. The organic portions were combined, dried over $MgSO_4$, filtered and evaporated to yield 4.5 g of a yellowish oil which, according to ^{1}H-NMR. spectrum, contained 76% of the desired product and 24% of starting material.

An analytically pure sample was prepared by flash chromatography [14] (SiO_2, column ∅ 50 mm, ether/petrol ether 35:65) which removed most of the starting material, followed by TLC. of about 300 mg of ester (*Merck* SiO_2 plate 2 mm, developed twice in ether/petrol ether 1:1) and Kugelrohr distillation. The portion collected at 130°/17 mbar was pure **2i**. – UV. (ethanol): 217 *S* (3660), 257 (230), 265 (160). – IR (film): 3080, 3010, 2980, 2940, 1780, 1775, 1755, 1595, 1495, 1490, 1430, 1340, 1270, 1195, 1175, 1145, 1030, 985, 860, 780, 690. – ^{1}H-NMR. (90 MHz, $CDCl_3$): 7.5–7.0 (*m*, 5 H arom. H); 3.4–3.1 (*m*, 2 H, H–C(2) and H–C(3)); 1.34 (*d*, J=5, 3 H, 3 H–C(4)). – ^{13}C-NMR. (22.63 MHz, 2.2M in $CDCl_3$): see *Table*.

$C_{10}H_{10}O_3$ (178.19) Calc. C 67.40 H 5.66% Found C 67.19 H 5.75%

3.8. *Phenyl (2*R*,3*S*)-2,3-epoxy-2-methylbutyrate* (**2j**). Phenyl 2-methylcrotonate (**2f**, 4 g, 22.7 mmol) was added to a solution of 5.87 g (90%, 34 mmol) *m*-chloroperbenzoic acid in 150 ml of CH_2Cl_2. The mixture was refluxed for 2 d (^{1}H-NMR. indicated complete epoxidation) and then extracted successively with 200 ml of 10% Na_2SO_3-solution and 200 ml of 5% $NaHCO_3$-solution. The aqueous phases were washed with 100 ml of CH_2Cl_2. The organic phases were worked up as in 3.7 and yielded crude **2j** as a yellowish oil (4.4 g, 100%). Kugelrohr distillation (130–140°/17 mbar) gave a colorless, analytically pure sample. – UV. (ethanol): 217 *S* (3600), 258 (300), 265 (210). – IR. (film): 3010, 2980, 2940, 1755, 1600, 1590, 1395, 1385, 1290, 1270, 1195, 1170, 1105, 870, 740, 690. – ^{1}H-NMR. (90 MHz, $CDCl_3$): 7.5–7.0 (*m*, 5 H, arom. H); 3.47 (*qa*, J=5.5, 1 H, H–C(3)); 1.63 (*s*, 3 H, CH_3); 1.40 (*d*, J=5.5, 3 H, 3 H–C(4)). – ^{13}C-NMR. (22.63 MHz, 1.8M in $CDCl_3$): see *Table*.

$C_{11}H_{12}O_3$ (192.21) Calc. C 68.73 H 6.29% Found C 68.42 H 6.40%

4. Chromones and related compounds. – 4.1. *Chromone* (**3a**). Commercial *(Fluka AG).* – ^{13}C-NMR. (22.63 MHz, 4.1M in $CDCl_3$): see *Table* (*cf.* [4], no. 3330).

4.2. *1-(2-Hydroxyphenyl)butane-1,3-dione* (**5b**). To 2-hydroxyacetophenone (**4**, *Fluka AG*, 10 g, 73.4 mmol) dissolved in ethyl acetate (27 g, 30 mmol) was added sodium in pieces (4 g, 174 mmol) [3]. A vigorous reaction occurred and a yellow precipitate was formed. After 30 min the reaction subsided. The mixture was then refluxed for 4 h; 15 ml of ethyl acetate had to be added to prevent the mixture from solidification. After cooling, 150 ml of abs. ether were added. The precipitated sodium salt was collected on a *Büchner* funnel, washed twice with abs. ether and dried. It was then suspended in 70 ml of 2N CH_3COOH and stirred vigorously. After 30 min the product was collected by filtration, washed three times with water and dried in a desiccator: 5.04 g (38.5%) of **5b**, m. p. of 90–91°. A small sample was recrystallized from toluene to give analytically pure colorless prisms, m. p. 92–93° ([3]: 90.5–91.5 (benzene)). – ^{1}H-NMR. (90 MHz, $CDCl_3$) *(diketo form):* 11.98 (*s*, 1 H, phenol. OH); 7.75–6.7 (*m*, 4 arom. H); 4.12 (*s*, 2 H, 2 H–C(2)); 2.33 (*s*, 3 H, 3 H–C(4)); *(enol. form):* 15.04 (br. *s*, 1 H, enol OH); 12.10 (*s*, 1 H, phenol. OH); 7.75–6.7 (*m*, 4 H, arom. H); 6.20 (*s*, 1 H, H–C(2)); 2,17 (*s*, 3 H, 3 H–C(4)); *(cyclic hemiacetal form):* 8.0–6.7 (*m*, 4 H, arom. H); 3.59 (br. *s*, 1 H, OH); 2.92 (*s*, 2 H, CH_2); 1.76 (*s*, 3 H, CH_3).

$C_{10}H_{10}O_3$ (178.19) Calc. C 67.40 H 5.66% Found C 67.39 H 5.68%

4.3. *2-Methylchromone* (**3b**). 1-(2-Hydroxyphenyl)butane-1,3-dione (**5b**, 2.0 g, 11.2 mmol), was warmed in 15 ml conc. hydrochloric acid on a steam bath for 5 min. The resulting clear, golden solution was poured onto 100 ml of ice-water and then neutralized with 90 ml of 2N NaOH. The crude chromone separated as a bulky white precipitate and was collected on a *Büchner* funnel. Extraction of the filtrate with two 200 ml portions of CH_2Cl_2 gave an additional 560 mg of **3b**. The crude crystals were taken up in 20 ml of CH_2Cl_2, which was washed with 20 ml of water, then dried over $MgSO_4$, filtered and evaporated to give 1.15 g of brownish crystals (total yield of crude product 1.71 g, 95%). These crystals were dissolved in 20 ml of hot cyclohexane and treated with charcoal. Upon cooling, the solution yielded 560 mg of pure **3b** as colorless plates, m. p. 70–71° ([15]: 72.5°). – ^{1}H-NMR. (90 MHz, $CDCl_3$): 8.18 (br. *d*, J=9, 1 H, H–C(5)); 7.8–7.2 (*m*, 3 H, arom. H); 6.16 (*s*, 1 H, H–C(3)); 2.36 (*s*, 3 H, CH_3). – ^{13}C-NMR. (22.63 MHz, 1.4M in $CDCl_3$): see *Table*.

$C_{10}H_8O_2$ (160.17) Calc. C 74.99 H 5.03% Found C 74.76 H 5.10%

4.4. *1-(2-Hydroxyphenyl)hexane-1,3-dione* (**5c**). To 2-hydroxyacetophenone (**4**, 10 g, 73 mmol) dissolved in methyl butyrate (**1c**, 47.7 g, 467 mmol) was added NaH (11 g of a 50% dispersion, *ca.* 230 mmol) in small portions over a period of 30 min. A yellow precipitate formed at once and turned orange after 10 min. The mixture was stirred at RT. for additional 3 h and was then poured on 200 ml of ice-water. The resulting yellow solution was extracted with 200 ml of CH_2Cl_2, which then was washed with 200 ml of water. The combined aqueous phases were acidified with 100 ml of 2N CH_3COOH, and the water insoluble material that separated was extracted with two 200 ml portions of CH_2Cl_2. These extracts were then washed with 100 ml of sat. $KHCO_3$-solution, combined, dried over $MgSO_4$, filtered and evaporated to yield 7.75 g (51%) of crude **5c** as an orange oil. TLC. revealed contamination with 2-propylchromone. A portion of this product (3.5 g) was flash chromatographed (SiO_2 column, 5 cm ∅, ether/petrol ether 35:65) [14] to yield 1.46 g of almost pure **5c**. It was distilled in a *Kugelrohr* at 135°/2 mbar to give 1.23 g of pure **5c** as a pale yellow oil. – UV. (ethanol): 213 (20'000), 252 (8200), 314 (5100). – IR. (film): 2970, 2940, 2880, 1720, 1690, 1610, 1580, 1490, 1460, 1440, 1300, 1245, 1220, 1160, 1035, 810, 760. – ^{1}H-NMR. (90 MHz, $CDCl_3$) *(diketo form):* 11.95 (*s*, 1 H, phenol. OH); 7.7–6.7 (*m*, 4 H, arom. H); 4.03 (*s*, 2 H, 2 H–C(2)); 2.53 (*t*, J=7, 2 H, 2 H–C(4)); 1.9–1.4 (*m*, 2 H, 2 H–C(5)); 1.1–0.8 (*m*, 3 H, 3 H–C(6)); *(enol form):* 15.0 (br. *s*, 1 H, enol. OH); 12.06 (*s*, 1 H, phenol. OH); 7.7–6.7 (*m*, 4 H, arom. H); 6.14 (*s*, 1 H, H–C(2)); 2.33 (*t*, J=7, 2 H, 2 H–C(4)); 1.9–1.4 (*m*, 2 H, 2 H–C(5)); 1.1–0.8 (*m*, 3 H, 3 H–C(6)); *(cyclic hemiacetal form):* 7.9–6.7 (*m*, 4 H, arom. H); 3.2 (br. *s*, 1 H, OH); 2.83 (*s*, 2 H, $H_2C(2)$); 2.9–2.4 (*m*, 4 H, CH_2CH_2); 1.1–0.8 (*m*, 3 H, CH_3).

$C_{12}H_{14}O_3$ (206.24) Calc. C 69.89 H 6.84% Found C 69.68 H 6.94%

4.5. *2-Propylchromone* (**3c**). 1-(2-Hydroxyphenyl)hexane-1,3-dione (**5c**, 3.7 g, 17.9 mmol) was stirred in 10 ml of onc. hydrochloric acid for 10 min on a steam bath. The resulting clear, golden solution was poured on 50 ml of ice-water, neutralized with 65 ml of 2N NaOH and then just reacidified with a few drops of 2N HCl. The crude chromone which had separated was extracted into two 100 ml portions of CH_2Cl_2. These were washed with 100 ml of sat. $KHCO_3$-solution, combined, dried over $MgSO_4$ and evaporated yielding the crude 2-propylchromone as a brownish oil (2.77 g, 82%). The product was dis-

tilled and the pure **3c** (1.70 g, 50%) collected at 104–105°/0.08 mbar ([16]: 120–123°/1.3 mbar). – ^{1}H-NMR. (90 MHz, $CDCl_3$): 8.18 (br. *d*, *J*=8, 1 H, H–C(5)); 7.8–7.2 (*m*, 3 H, arom. H); 6.17 (*s*, 1 H, H–C(3)); 2.58 (*t*, *J*=7, 2 H, 2H–C(1′)); 1.76 (*sextet*, *J*=7, 2 H, 2 H–C(2′)); 1.02 (*t*, *J*=7, 3 H, 3 H–C(3′)). – ^{13}C-NMR. (22.63 MHz, 2.0M in $CDCl_3$): see *Table*.

$C_{12}H_{12}O_2$ (188.23) Calc C 76.57 H 6.43% Found C 76.38 H 6.54%

4.6. *1-(2-Hydroxyphenyl)-4-methylhexane-1,3-dione* (**5d**). To a vigorously stirred mixture of 2-hydroxyacetophenone (**4**, 5.62 g, 41 mmol) and methyl 2-methylbutyrate (**1d**, 26.55 g, 228 mmol) was added NaH (6.37 g of 50% dispersion, 132 mmol) in small portions over a period of 15 min. During this time a vigorous exothermic reaction occurred, hydrogen was evolved and a yellow precipitate formed. The mixture almost solidified. After the addition of NaH the reaction mixture was warmed on a steam bath for 30 min and then stirred at RT. overnight. The syrupy brown product, which contained some precipitated salts, was poured into 500 ml of ice-water, which then was extracted once with 250 ml of CH_2Cl_2. The aqueous phase was then acidified with 85 ml of 2N CH_3COOH (yielding *ca.* pH 5). The organic compound which separated was extracted with 3 × 250 ml portions of CH_2Cl_2 which were washed with 200 ml of sat. aqueous $KHCO_3$-solution, combined, dried with $MgSO_4$, filtered and evaporated. The brown residue (7.14 g, 79%) was distilled i. V. The fraction boiling at 114–120°/0.7 mbar was collected to give 5.58 g (61.8%) of **5d**. – UV. (ethanol): 203 (13′800), 210 (16′500), 220 (19′500), 261 (6800), 318 (7800), 342 (7300). – IR. (film): 3500–2000 br., 2960, 2930, 2870, 1600, 1570, 1485, 1290, 750. – ^{1}H-NMR. (60 MHz, $CDCl_3$): 15.15 (br. *s*, 0.87 H, enol. OH); 12.10 (br. *s*, 0.87 H, phenol. OH in enol form); 12.05 (br. *s*, 0.13 H, phenol. OH in diketone form); 7.8–7.2 (*m*, 2 H, H–C(4′) and H–C(6′)); 7.1–6.7 (*m*, 2 H, H–C(3′) and H–C(5′)); 6.18 (*s*, 0.87 H, 2H–C(2) in enol form); 4.09 (*s*, 0.26 H, 2H–C(2) in diketone form); 2.6–2.0 (*m*, 1 H, CH); 2.0–1.3 (*m*, 2 H, CH_2); 1.19 (*d*, *J*=7, 3 H, CH_3); 0.92 (*t*, *J*=7, 3 H, CH_3).

$C_{13}H_{16}O_3$ (220.27) Calc. C 70.89 H 7.32% Found C 70.64 H 7.34%

4.7. *2-(1-Methylpropyl)chromone* (**3d**). The diketone **5d** (4.3 g, 19.5 mmol) was added to conc. hydrochloric acid (30 ml) and the mixture stirred by hand with a glass rod on the steam bath. After 3 min a clear yellow solution was obtained, which was stirred at RT. for another 2 min and then poured into 100 ml of ice-water. The mixture was neutralized with *ca.* 45 ml of 33% NaOH-solution and then just reacidified with a few drops of 2N HCl. The oily material that separated was extracted wit 2 × 200 ml portions of CH_2Cl_2, which were washed once with 200 ml of water. The organic portions were then combined, dried over $MgSO_4$, filtered and evaporated. A yellow oil (4.26 g) resulted, which was purified by distillation i. V. The fraction boiling at 120–124°/0.3 mbar was collected and yielded 2.77 g (70.0%) of pure **3d**. – UV. (ethanol): 194 (14′100), 200 (14′500), 223 (23′900), 243 *S* (9300), 262 *S* (7900), 294 (7900), 299 *S* (7600). – IR. (film): 3060, 2960, 2930, 2870, 1650, 1570, 1460, 1380, 1360, 1215, 1115, 930, 770, 750. – ^{1}H-NMR. (60 MHz, $CDCl_3$): 8.12 (br. *d*, *J*=8, 1 H, H–C(5)); 7.75–7.1 (*m*, 3 H arom. H); 6.12 (*s*, 1 H, H–C(3)); 2.60 (*sextet*, *J*=7, 1 H, H–C(1′)); 2.1–1.4 (*m*, 2 H, 2 H–C(2′)); 1.29 (*d*, *J*=7, 3 H, CH_3); 0.92 (*t*, *J*=7, 3 H, CH_3). – ^{13}C-NMR. (22.63 MHz, 2.0M in $CDCl_3$): see *Table*.

$C_{13}H_{14}O_2$ (202.25) Calc. C 77.20 H 6.98% Found C 77.20 H 7.11%

4.8. *(4E)-1-(2-Hydroxyphenyl)-4-hexene-1,3-dione* (**5e**). To a solution of 2-hydroxyacetophenone (**4**, 10 g, 73.4 mmol) in 200 ml of toluene was added NaH (11.9 g, 50% dispersion, 240 mmol) under vigorous stirring. The resulting suspension of the yellow sodium salt was brought to reflux. Methyl crotonate (**1e**, 18.9 g, 189 mmol) was added during the next 2.5 h. The suspension turned orange-red and was refluxed for an additional 24 h. After cooling to RT., 300 ml of ice-water were added under stirring. Then, the phases were separated and the toluene layer was washed with 50 ml of water. The aqueous phases were combined and acidified with 200 ml of 2N CH_3COOH. The orange oily precipitate that formed was extracted into two 200 ml portions of CH_2Cl_2, which were washed with 200 ml of sat. $KHCO_3$-solution, then combined, dried over $MgSO_4$, filtered and concentrated to give 16 g of a brown syrup. This material was chromatographed on a silica gel column (300 g SiO_2 60, *Merck*, 63–200 μm, 150 ml fractions) with CH_2Cl_2. Fractions 4–7 gave 702 mg of **5e**, which was recrystallized twice from ethanol. Yellow needles m. p. 109–111° (390 mg, 2.6%). – UV. (ethanol): 221 *S* (12′600), 226 (12′900), 231 *S* (11′300), 251 *S* (5100), 275 *S* (3300), 322 *S* (15′000), 334 (19′000), 360, (24′000). – IR. (KBr): 3040, 2940, 2920, 1650, 1590, 1570, I485, 1435, 1420, 1370, 1330, 1295, 1245, 1215, 1180, 1170, 1160, 1130, 1100, 1060, 955, 865, 810, 750, 685, 635. – ^{1}H-NMR. (90 MHz, $CDCl_3$) (only *enol form*): 14.62 (br. *s*, 1 H, enol. OH), 12.18 (*s*, 1 H, phenol. OH); 7.75–6.65 (*m*, 5 H, arom. H and H–C(5)); 6.11 (*s*, 1 H, H–C(2)); 5.95 (*d* × *qa*, *J*=16 and 2, 1H, H–C(4)); 1.92 (*d* × *d*, *J*=7 and 2, 3 H, 3H–C(6)).

$C_{12}H_{12}O_3$ (204.23) Calc. C 70.58 H 5.92% Found C 70.31 H 5.91%

4.9. *2-[(1E)-1-Propenyl]chromone* (**3e**). The diketone **5e** (180 mg, 0.88 mmol) was stirred with 2 ml of conc. hydrochloric acid on a steam bath for 7 min. A clear, yellow solution resulted, which was poured in 10 ml of ice-water. The mixture was neutralized with 2N NaOH, reacidified with a few drops of 2N HCl, and the crude chromone was extracted into two 50 ml portions of CH_2Cl_2. These were washed with 50 ml of water, combined, dried over $MgSO_4$, filtered and evaporated to give 160 mg (97%) of **3e** as a colorless oil, which solidified upon standing. The product was dissolved in cyclohexane and heated briefly together with some charcoal. The solution was filtered and concentrated somewhat. After inocculation, 90 mg (55%) of colorless needles could be isolated, m. p. 70–72°. – UV. (ethanol): 215 (16'000), 235 *S* (11'400), 247 (17'400), 254 (19'500), 290 (20'600), 303 *S* (16'600). – IR. (KBr): 3040, 1630, 1605, 1555, 1460, 1385, 1305, 1295, 1240, 1220, 1120, 1025, 975, 960, 920, 890, 870, 780, 760, 680. – ^{1}H-NMR. (90 MHz, $CDCl_3$): 8.15 (br. *d*, *J*=8, 1 H, H–C(5)); 7.75–7.2 (*m*, 3 H, arom. H); 6.83 (*d*×*qa*, *J*=15 and 7, 1 H, H–C(2')); 6.14 (*d*×*qa*, *J*=15 and 2, 1 H, H–C(1')); 6.13 (*s*, 1 H, H–C(2)); 1.95 (*d*×*d*, *J*=7 and 2, 3 H, H–C(3')). – ^{13}C-NMR. (22.63 MHz, 0.7M in $CDCl_3$): see *Table*.

$C_{12}H_{10}O_2$ (186.21) Calc. C 77.40 H 5.41% Found C 77.32 H 5.45%

4.10. *(4E)-1-(2-Hydroxyphenyl)-4-methyl-4-hexene-1,3-dione* (**5f**). To 2-hydroxyacetophenone (**4**, 5 g, 36.7 mmol) dissolved in 100 ml of toluene was added NaH (6.3 g of 55% dispersion, *ca.* 150 mmol), whereupon a yellow precipitate formed. The mixture was heated to reflux and stirred vigorously. Then, 10 g (87.6 mmol) of **1f** were added over the total reflux period of 8 h. Stirring was continued at RT. overnight. The syrupy reaction mixture was poured on 200 ml of ice-water and stirred vigorously. The phases were separated and the aqueous layer acidified with 70 ml of 2N CH_3COOH. The water insoluble material that separated was extracted with two 250 ml portions of CH_2Cl_2, which were washed once with 250 ml of sat. aqueous $KHCO_3$-solution. The organic phases were combined, dried over $MgSO_4$, filtered and evaporated. A yellow oil resulted (6.5 g, 81%), which was purified by vacuum distillation in a *Kugelrohr*. The portion passing at 145–175°/0.8 mbar (2.77 g, 34.5%) was collected. It solidified after standing at RT. A small sample was recrystallized from ethanol/water: thin pale yellow plates of **5f**, m. p. 62–66°. – UV. (ethanol): 221 (16'000), 235 *S* (9500), 253 *S* (7400), 333 *S* (14'200), 359 (17'800). – IR. (KBr): 3500–2000 br., 3080, 2980, 1645, 1610, 1575, 1480, 1290, 1265, 1190, 1030, 870, 750, 730, 720. – ^{1}H-NMR. (60 MHz, $CDCl_3$): 15.15 (br. *s*, 0.8 H, enol. OH); 12.10 ppm (br. *s*, 0.8 H, phenol. OH in enol form); 12.02 (br. *s*, 0.2 H, phenol OH in diketone form); 7.75–7.2 (*m*, 2 H, H–C(4') and H–C(6')); 7.0–6.6 (*m*, 3 H, H–C(3'), H–C(5') and H–C(5)); 6.30 (*s*, 0.8 H, H–C(2) in enol form); 4.25 (*s*, 0.4 H, 2H–C(2) in diketone form); 1.9–1.7 (*m*, 6 H, 2 CH_3).

$C_{13}H_{14}O_3$ (218.25) Calc. C 71.54 H 6.47% Found C 71.42 H 6.65%

4.11. *2-[(1E)-1-Methyl-1-propenyl]chromone* (**3f**). The diketone **5f** (1.51 g, 6.9 mmol) was added to 15 ml of conc. hydrochloric acid and stirred at RT. for 7 min. The mixture was then heated briefly on a steam bath, whereupon a clear dark yellow solution was obtained. This solution was poured onto 100 ml of ice-water and the product that separated was extracted with two 200 ml portions of CH_2Cl_2. The extracts were washed once with 200 ml sat. aqueous $KHCO_3$-solution, combined, dried over $MgSO_4$, filtered and evaporated. A yellow oil resulted (1.35 g, 98%), which solidified after standing overnight at RT. A small sample was recrystallized three times from benzene/petrol ether to give almost colorless prisms of **3f**, m. p. 60–61°. – UV. (ethanol): 214 (16'500), 247 (13'900), 254 (13'800), 292 (18'800). – IR. (KBr): 3050, 2910, 1630, 1555, 1460, 1360, 1125, 820, 770, 760, 745, 595. – ^{1}H-NMR. (60 MHz, $CDCl_3$): 8.13 (br. *d*, *J*=8, 1 H, H–C(5)); 7.8–7.1 (*m*, 3 H, arom. H); 6.74 (br. *qa*, *J*=7, 1 H, H–C(2')); 6.27 (*s*, 1 H, H–C(3)); 1.92 (*s*, 3 H, CH_3); 1.86 (*d*, *J*=7, 3 H, CH_3). – ^{13}C-NMR. (22.63 MHz, 2.1M in $CDCl_3$): see *Table*.

$C_{13}H_{12}O_2$ (200.24) Calc. C 77.98 H 6.04% Found C 77.81 H 6.14%

4.12. *2-[(1E,3E)-1-Methyl-1,3-pentadienyl]chromone* (**3g**). See [6]. – ^{13}C-NMR. (22.63 MHz, *ca.* 2.2M in $CDCl_3$): see *Table* (from [6]).

4.13. *Flavone* (**3h**). Commercial *(Fluka AG)*. – ^{13}C-NMR. (22.63 MHz, 1.2M in $CDCl_3$): see *Table* (*cf.* [4], no. 3329).

4.14. *2-[(1R*,2S*)-1,2-Epoxypropyl]chromone* (**3i**). 2-[(1*E*)-1-propenyl]-chromone (**3e**, 150 mg, 0.81 mmol) was dissolved in a dried ($MgSO_4$) solution of *m*-chloroperbenzoic acid (232 mg, 90%, 1.21 mmol) in 2.3 ml of CH_2Cl_2. The mixture was refluxed for 2 d, when ^{1}H-NMR. spectroscopy indicated 80–90% epoxidation. The reaction mixture was diluted with 40 ml of CH_2Cl_2 and extracted successively with 30 ml of 10% Na_2SO_3-solution and 30 ml of 5% $NaHCO_3$-solution. The aqueous phases were washed with 30 ml of CH_2Cl_2. The organic layers were combined, dried over $MgSO_4$, filtered and evaporated to give

3i as a yellow oil (150 mg, 92%). This material was chromatographed on a PSC plate (*Merck*, SiO_2, 2 mm, developed twice in ether/petrol ether 1:1). Elution of the product from the adsorbent was achieved with CH_2Cl_2 and ether, giving each 30 mg of an almost colorless oil, which solidified on standing. The portion eluted with CH_2Cl_2 was recrystallized from cyclohexane to yield pure **3i** as colorless leaflets, m. p. 84–86°. – UV. (ethanol): 228 (22'500), 249 *S* (9200), 263 *S* (8100), 296 (7500), 302 *S* (7200). – IR. (KBr): 3080, 3020, 2980, 1650, 1635, 1600, 1575, 1470, 1445, 1395, 1380, 1330, 1125, 1025, 1020, 990, 950, 840, 785, 770, 765, 750. – ^{1}H-NMR. (90 MHz, $CDCl_3$): 8.17 (br. *d*, J=8, 1 H, H–C(5)); 7.8–7.2 (*m*, 3 H, arom. H); 6.35 (*s*, 1 H, H–C(3)); 3.49 (*d*, J=2, 1 H, H–C(1')); 3.37 (*qa* × *d*, J=5 and 2, 1 H, H–C(2')); 1.50 (*d*, J=5, 3 H, 3 H–C(3')). – ^{13}C-NMR. (22.63 MHz, 0.7M in $CDCl_3$): see *Table*.

$C_{12}H_{10}O_3$ (202.21) Calc. C 71.28 H 4.98% Found C 71.33 H 5.07%

4.15. *2-[(1R*,2S*)-1,2-epoxy-1-methylpropyl]chromone* (**3j**). The olefinic chromone **3f** (1.12 g, 5.6 mmol) was oxidized with *m*-chloroperbenzoic acid (1.6 g of ca. 90%, *Fluka AG*, *ca.* 8.4 mmol) in refluxing CH_2Cl_2 (50 ml) for 19 h. At that time the ^{1}H-NMR. spectrum of the reaction mixture indicated complete epoxidation. The solution was allowed to cool, and was then washed with 50 ml of 20% Na_2SO_3-solution, 50 ml of sat. $KHCO_3$-solution and 50 ml of water. The emulsions that formed occasionally were broken up by the addition of some NaCl. The aqueous layers were washed twice with 50 ml of CH_2Cl_2. The organic solutions were combined, dried over $MgSO_4$, filtered and evaporated to give 1.26 g of a yellow syrup. *Kugelrohr* distillation at 145–160°/0.47 mbar yielded 920 mg (76%) of **3j** as a yellow, very viscous oil. A sample of this product (250 mg) was subjected to TLC. (SiO_2 plate *Merck*, 2 mm, two successive developments in ether/petrol ether 1:1). The zone containing the main product was scraped out and the chromone eluted from the silica gel with 3 × 10 ml portions of CH_2Cl_2. After removal of the solvent, the residue solidified. It could be recrystallized from cyclohexane to give colorless crystals, m. p. 72–74°. – UV. (ethanol): 227 (23'000), 249 *S* (8900), 262 *S* (7800), 295 (7500), 300 (7300). – IR. (KBr): 3000, 2980, 2930, 1640, 1600, 1570, 1460, 1385, 1370, 1360, 1210, 1120, 1065, 950, 860, 810, 780, 760. – ^{1}H-NMR. (90 MHz, $CDCl_3$): 8.18 (br. *d*, J=8, 1 H, H–C(5)); 7.8–7.2 (*m*, 3 H, arom. H); 6.40 (*s*, 1 H, H–C(3)); 3.25 (*qa*, J=6, 1 H, H–C(2')); 1.67 (*s*, 3 H, CH_3); 1.46 (*d*, J=6, 3 H, CH_3). – ^{13}C-NMR. (22.63 MHz, *ca.* 1.5M in $CDCl_3$): see *Table*.

$C_{13}H_{12}O_3$ (216.25) Calc. C 72.21 H 5.59% Found C 71.93 H 5.64%

4.16. *2[(1R*,2S*,3R*,4S*)-1,2:3,4-Diepoxy-1-methylpentyl]chromone* (**3k**). See [6]. – ^{13}C-NMR. (22.63 MHz, *ca.* 2,5M in $CDCl_3$): see *Table* (from [6]).

4.17. *2-[(1R*,2S*,3S*,4R*)-1,2:3,4-Diepoxy-1-methylpentyl]chromone* (**3l**). See [6]. – ^{13}C-NMR. (22.63 MHz, *ca.* 1.4M in $CDCl_3$): see *Table* (from [6]).

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