# Oxidation Reactions of Marchantin A Trimethyl Ether and Some Aromatic Compounds using *m*-Chloroperbenzoic Acid. Formation of Muconic Acid Ester and *m*-Chlorobenzoate

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On treatment with *m*-chloroperbenzoic acid, dihydroeugenol methyl ether and marchantin A trimethyl ether afford muconic acid ester derivatives by oxidation of the aromatic ring as well as hydroxylated derivatives; the *m*-chlorobenzoate of the dihydroeugenol derivative is also observed for the former.

We have been interested in oxidation reactions of various types of natural and unnatural substances using *m*-chloroperbenzoic acid (*m*-CPBA),[1–10] because the procedure is easy and safe for almost all compounds including arenes. We have investigated the oxidation reaction of related aromatic compounds including marchantin A, a macrocyclic bis(bibenzyl) isolated from the liverwort *Marchantia polymorpha* and related species,[11] and have found that the muconic acid ester derivative and further degraded compounds were produced as well as hydroxylated compounds.[12] Oxidation of dihydroeugenol methyl ether was also studied, and found to afford the *m*-chlorobenzoate of its derivative, the first example of formation of the *m*-chlorobenzoate.

Dihydroeugenol methyl ether **1** was treated with *m*-CPBA to give products **2**–**5**. An X-ray analysis of **4** was performed and its structure was established as depicted in Fig. 1.[12] This is the first example of isolation of the *m*-chlorobenzoate derivative from reaction using *m*-CPBA.

Marchantin A trimethyl ether **6** was subjected to reaction with *m*-CPBA to give products **7**–**10**. From the IR and MS spectra of **7** one hydroxy group was introduced into either aromatic ring. NMR analyses suggested at rings A, B and D were unchanged, while one of the ring C protons disappeared. Because the proton at H-3′ was detected for compound **7** as a singlet, the position of the hydroxy group must be at C-5′ and

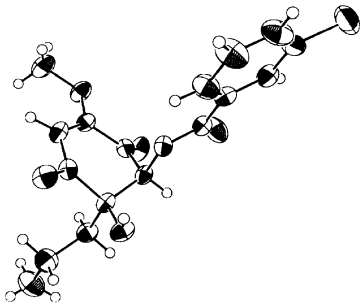
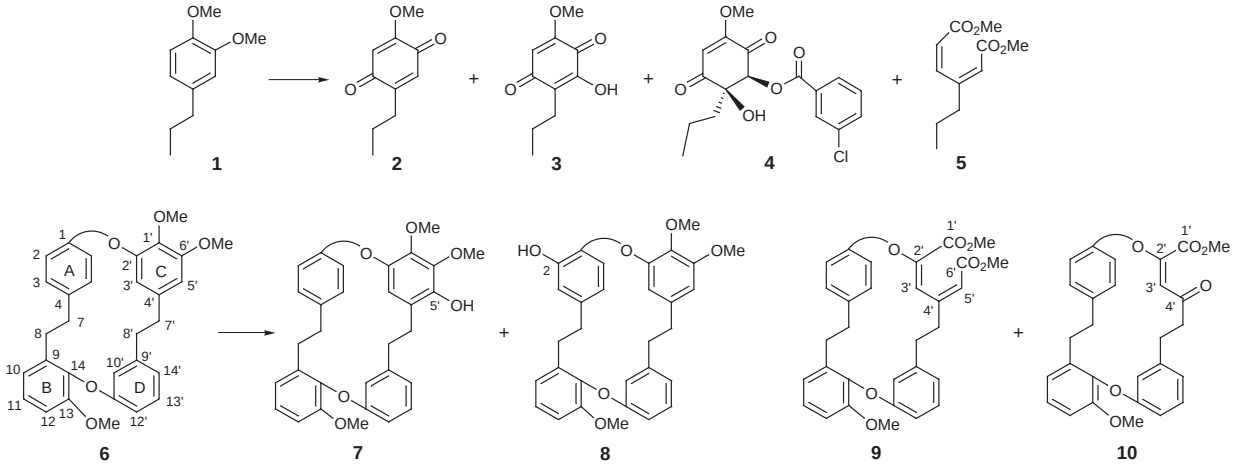


**Fig 1** ORTEP drawing of compound **4**

hence the structure of **7** was established as shown. One hydroxy group was introduced into **8** as for **7**, which was supported by its IR spectrum and detailed NMR analyses. The NMR spectrum of **9** suggested that the proton systems for rings A, B and D were almost the same as in **6**, while the signals of ring C were somewhat different from those of **6**, indicating that degradation occurred in ring C. The structure of **9** was established as shown by extensive NMR analyses. There were only two methoxy groups, one of which should be an ester, for **10**, which contains three less carbons than **9**. It was concluded that compound **10** is the degraded keto ester as shown.



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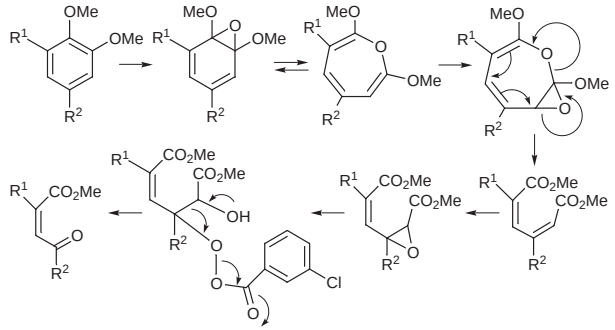
A possible mechanism for the formation of muconic acid ester and keto ester is shown in Scheme 1.



**Scheme 1** Possible reaction mechanism for formation of muconic acid ester and keto ester

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Techniques used: IR, $^{1}H$ and $^{13}C$ NMR

References: 25

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## References cited in this synopsis

1 M. Tori, R. Matsuda and Y. Asakawa, *Chem. Lett.*, 1985, 167.
2 M. Tori, R. Matsuda and Y. Asakawa, *Tetrahedron Lett.*, 1985, **26**, 227.
3 M. Tori, M. Sono and Y. Asakawa, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 2669.
4 M. Tori, R. Matsuda and Y. Asakawa, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 2523.
5 M. Tori, R. Matsuda and Y. Asakawa, *Tetrahedron*, 1986, **42**, 1275.
6 Y. Asakawa, R. Matsuda and M. Tori, *Experientia, 1986,* **42**, 201.
7 M. Tori, R. Matsuda, M. Sono, Y. Kohama and Y. Asakawa, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 2103.
8 Y. Asakawa, R. Matsuda, M. Tori and T. Hashimoto, *Phytochemistry*, 1988, **27**, 3861.
9 M. Tori, M. Sono and Y. Asakawa, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 1770.
10 Y. Asakawa, R. Matsuda, M. Tori and M. Sono, *J. Org. Chem.*, 1988, **53**, 5453.
11 Y. Asakawa, *Prog. Chem. Org. Nat. Prod.,* 1982, **42**, 1; 1995, **65**, 1.
12 M. Tori, M. Sono, M. Toyota and Y. Asakawa, *Heterocycles*, 1998, **47**, 647.