

## Reaction of Fucosterol 24,28-Epoxyde with Boron Trifluoride Etherate

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**Summary** Brief treatment of fucosterol 24,28-epoxyde with  $\text{BF}_3$  etherate gives desmosterol by a fragmentation reaction, which could be a model reaction for biological dealkylation of the sterol side-chain in insects.

In continuation of studies on the chemical reactivity of the sterol side-chain,<sup>1</sup> we have found a novel fragmentation reaction of fucosterol 24,28-epoxyde.

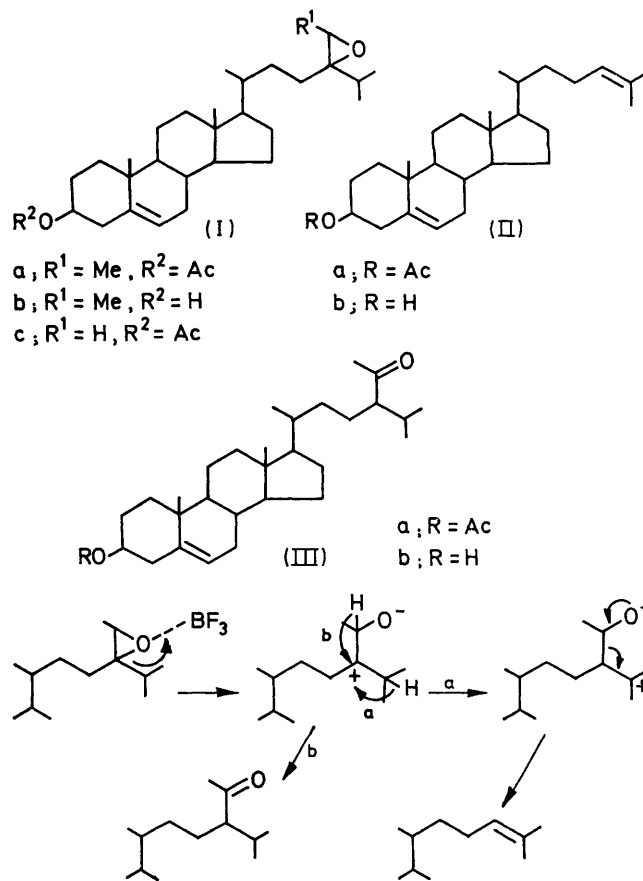
Selective epoxidation of fucosteryl acetate with *m*-chloroperbenzoic acid (1 equiv.) in chloroform at 0°, gave fucosteryl acetate 24,28-epoxyde (Ia), m.p. 101–103°, in 75% yield: n.m.r.( $\text{CDCl}_3$ ),  $\delta$  0.67(3H, s), 0.85–0.95(9H, m), 1.01(3H, s), 1.25(3H, d, *J* 6Hz), 2.02(3H, s), 2.88(1H, q, *J* 6Hz), 4.60(1H, m), and 5.35 p.p.m.(1H, m); *m/e*, 410, 410 (*M* – AcOH). When the epoxyde (Ia) (270 mg) was treated with  $\text{BF}_3$  etherate (0.5 ml) in anhydrous benzene (5 ml) at room temperature for 10 s, at least two compounds were produced, as revealed by g.l.c. analysis on 1.5% OV-1. Each compound was separated and purified by column chromatography on silicic acid.

One major product (35%) had a much shorter g.l.c. retention time than (Ia), and was definitely identified with desmosteryl acetate (IIa) by direct comparison with an authentic sample in respect of m.p., g.l.c., i.r., n.m.r., and mass spectra. The structure of another product (45%), m.p. 130–132°, was determined as 3 $\beta$ -acetoxystigmast-5-en-28-one (IIIa).

Similarly, fucosterol 24,28-epoxyde (Ib), m.p. 107–109°, afforded desmosterol (IIb) (30%) and the methyl ketone (IIIb) (46%), m.p. 120–125°. On the other hand, 24-methylenecholesteryl acetate 24,28-epoxyde (Ic), m.p. 134–136°, gave no detectable yield of (IIa) under the same reaction conditions.

A possible mechanism for the conversion of (I) into (II) and (III) may be as shown below. A similar mechanism for reactions of epoxydes with  $\text{BF}_3$  has been reported by Coxon<sup>2–4</sup> and Guest.<sup>5</sup>

Plant-eating insects obtain 24-ethylcholesterol ( $\beta$ -sitosterol) from their food and they can convert it into cholesterol.<sup>6–8</sup> Recently, desmosterol<sup>9,10</sup> and fucosterol<sup>11,12</sup> have



been identified as intermediates in this conversion. The ready transformation of (I) into (II), described above, seems to suggest that this epoxyde could play an important role in the biological dealkylation. Biogenetic experiments to clarify this hypothesis are in progress in this laboratory.

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