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Title

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Permalink

<https://escholarship.org/uc/item/3zz7p346>

Journal

Chemical Communications, 0(15)

ISSN

1359-7345

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Publication Date

1973

DOI

10.1039/c39730000530

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Identity of Ergosterol '5 β ,8 β -Peroxide'

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Summary Ergosterol '5 β ,8 β -peroxide' has been identified as 9,11-dehydroergosterol peroxide.

THE recent report¹ that ergosterol peroxide (I), long accepted as being a single, pure compound, is in fact a mixture of the 5 α ,8 α - and 5 β ,8 β -endo-peroxides (I) and (II) in the ratio 84:16 requires amendment.

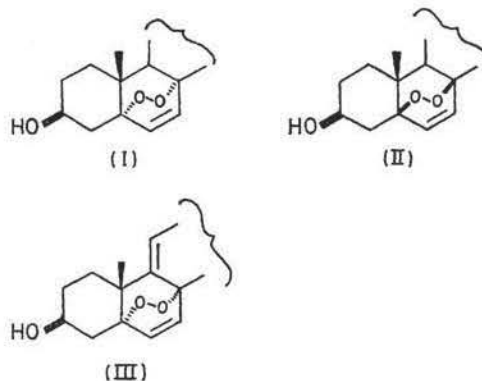
Samples of ergosterol peroxide (I) prepared at Imperial College from recrystallised ergosterol by photo-oxidation (singlet oxygen) and aminium radical-cation catalysed oxygenation² (triplet oxygen) contained only ergosterol peroxide (I). No trace of a second compound could be found by 220 MHz n.m.r. spectroscopy.

A comparison of pure ergosterol peroxide (I), the claimed mixture [(I) + (II)] and 9,11-dehydroergosterol peroxide (III) is instructive.

	Ergosterol peroxide (I)	[(I) + (II)] (84:16)	(III)
M.p.	176–178°	167–171°	161–165°
$[\alpha]_D^{21.5}$ (CHCl ₃)	–32.9°	–13.5°	+80°

A mixture of 16% (III) and 84% (I), prepared from the pure compounds, had $[\alpha]_D -14.2^\circ$. Similarly the n.m.r. spectrum of 16% (III) and 84% (I) is identical with that reported for [(I) + (II)]. Acetylation of a specimen of the ergosterol peroxide [(I) + (II)] prepared earlier¹ at Irvine by oxidation of ergosterol (singlet oxygen) and p.l.c. of the

product against ergosterol peroxide acetate and 9,11-dehydroergosterol peroxide acetate (AgNO₃-SiO₂ plates) demonstrated the presence of 9,11-dehydroergosterol peroxide acetate. The mass spectrum of [(I) + (II)] shows a strong $M-2$ 428 m/e corresponding in relative intensity to approximately 16% of (III).



These data conclusively show that the supposed ergosterol 5 β ,8 β -peroxide (II) is in reality the long known 9,11-dehydroergosterol peroxide.

(Received, 1st June 1973; Com. 784.)

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¹ J. Arditti, R. Ernst, M. H. Fisch, and B. H. Flick, *J.C.S. Chem. Comm.*, 1972, 1217.

² D. H. R. Barton, G. Leclercq, P. D. Magnus, and I. D. Menzies, *J.C.S. Chem. Comm.*, 1972, 446.