

Diacetoxyscirpenol and some Related Compounds

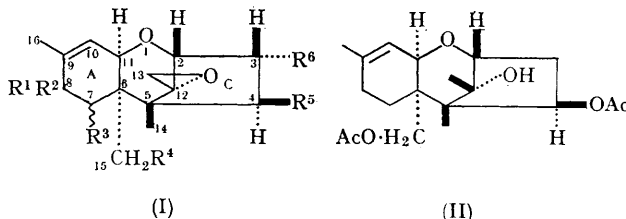
By A. W. DAWKINS, JOHN FREDERICK GROVE, and B. K. TIDD

(Imperial Chemical Industries Limited, Akers Research Laboratories, The Frythe, Welwyn, Herts; London School of Hygiene and Tropical Medicine, W.C.1. Present addresses: (A.W.D.) Marchon Products Ltd., Whitehaven, Cumberland; (J.F.G.) Tropical Products Institute, London, W.C.1. (B.K.T.) Natural Rubber Producers Association, Welwyn Garden City, Hertfordshire)

THE structure and relative configuration of diacetoxyscirpenol, $C_{19}H_{26}O_7$, the principal phytotoxic metabolic product of the plant parasitic fungus *Fusarium equiseti*,¹ has been established as (Ia); the minor product $C_{19}H_{24}O_9$, m.p. 135–136°, is the conjugated enone (Ie).

The skeleton of diacetoxyscirpenol was shown¹ to be tetracyclic with two ether linkages. The proton magnetic resonance spectrum showed one of these to be present in an ethylene oxide ring (τ 7.02, 7.29; $J = 4c./sec.$), and was indicative of two tertiary C-Me groups (cf.¹) and a *trans* α -glycol grouping

	R ¹ R ²	R ³	R ⁴	R ⁵	R ⁶
(I)a	H ₂	H	OAc	OAc	OH
b	H ₂	H	OH	OH	OH
c	H ₂	H	OH	OH	H
d	H ₂	H	H	OH	H
e	O	OH	OAc	OAc	OH
f	O	H	H	OH	H



¹ P. W. Brian, A. W. Dawkins, J. F. Grove, H. G. Hemming, D. Lowe, and G. L. F. Norris, *J. Exp. Bot.*, 1961, 12, 1.

(τ 4.8, 5.9; $J_{3,4} = 3$ c./sec.) in scirpentriol (Ib), the $C_{15}H_{22}O_5$ product of alkaline hydrolysis, which did not undergo fission with periodate. Consistent with this relative configuration, the toluene-*p*-sulphonate of diacetoxyscirpenol did not undergo elimination in the presence of collidine: hydrogenolysis with lithium aluminium hydride was accompanied, without skeletal rearrangement, by simultaneous opening of the 12,13-epoxide. Reacetylation of the product gave the diacetate (II),² a transformation product† of the $C_{15}H_{22}O_4$ alcohol verrucarol, now formulated as (Ic).³

The proton magnetic resonance spectrum of the enone (Ie) showed chemical shifts similar to, and coupling constants identical with, those attributed to hydrogens at positions 2, 3, 4, 11, 13 and 15 in diacetoxyscirpenol and was consistent with the *cis*-fusion of rings A/B and with a *cis*-relationship of the 12, 13-epoxide and 5-methyl group. Mild alkaline hydrolysis gave a tetrahydroxy-ketone, $C_{15}H_{20}O_7$.

† We are indebted to Professor Ch. Tamm, Institut für Organische Chemie der Universität, Basel, for an authentic specimen. Subsequently we were informed by Prof. Tamm that workers at Sandoz A. G. Basel had, independently, deduced the structure of diacetoxyscirpenol and we agreed to the simultaneous publication of our findings (see preceding paper).

² J. Gutzwiller and Ch. Tamm, *Helv. Chim. Acta*, 1963, **46**, 1786.

³ J. Gutzwiller, R. Mauli, H. P. Sigg and Ch. Tamm, *Helv. Chim. Acta*, 1964, **47**, 2234.

⁴ G. G. Freeman, J. E. Gill and W. S. Waring, *J.*, 1959, 1105; J. Fishman, E. R. H. Jones, G. Lowe, and M. C. Whiting, *J.*, 1960, 3948.

⁵ E. Harri, W. Loeffler, H. P. Sigg, H. Stahelin, Ch. Stoll, Ch. Tamm, and D. Weisinger, *Helv. Chim. Acta*, 1962, **45**, 839; Ch. Tamm and J. Gutzwiller, *Helv. Chim. Acta*, 1962, **45**, 1726.

⁶ W. O. Godtfredsen and S. Vangedal, *Proc. Chem. Soc.*, 1964, 188.

⁷ S. Abrahamsson and B. Nilsson, *ibid.*

Verrucarol and the $C_{15}H_{20}O_4$ hydroxy-ketone trichothecolone⁴ (If), hydrolysis products respectively of verrucarin A,⁵ from *Myrothecium vridum* and *M. verrucaria*, and of trichothecin, from *Trichothecium roseum*, have been interconnected⁸ and related⁶ to roridin C (Id), a minor metabolic product of *M. vridum* and its acetyl derivative, trichodermin, from a *Trichoderma sp.* The structure and relative configuration of roridin C has been established unequivocally by X-ray crystallographic analysis.⁷

The chemical reactions^{2,3,5} of these sesquiterpene alcohols, produced by diverse fungi, are profoundly influenced by the presence of absence of an 8-keto-group which determines the nature of the skeletal rearrangement following acid-catalysed opening of the ethylene oxide ring. Both types of compound are produced by *F. equiseti*.

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