Novel Germination Inhibitors from *Aegilops ovata L.*

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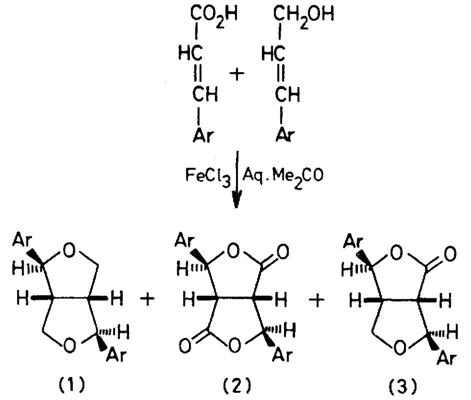
Summary A synthetic approach has led to a revision of structure for the germination inhibitor of *Aegilops ovata L.*, from which a second lignan of the same series has now been isolated and identified.

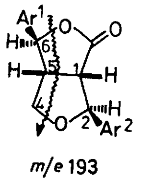
Naturally occurring germination inhibitors are attracting increasing attention;[1,2] particularly those of cinnamic acid origin are already established as having such a biological activity.[2] Earlier a novel lignan† containing this C_6-C_3 unit had been isolated from *Aegilops ovata L.* and found to be a potent germination inhibitor in the presence of light.[3] Subsequently similar lignans have been reported.[4] Since controversy over the proposed structures has recently arisen,[5] we report evidence leading to the revised structure as a consequence of independent synthesis.



(1) (2) (3)

Ar = 3-Methoxy-4-hydroxyphenyl

The 2,6-biaryl structure instead of the 2,4-biaryl pattern became apparent from the oxidative phenolic coupling[6] of ferulic acid with coniferyl alcohol. Three compounds were isolated, two of which [(**1**) and (**2**)] were the expected products.[7,8] The epoxy-lactone (**3**) was identical in all respects to the naturally occurring compound, both having the same i.r., n.m.r., and mass spectra as well as identical R_f on t.l.c. Both acetylated products had m.p. (and mixed m.p.) 166—168 °C. Reassignment of the stereochemistry of the hydrogen atoms as being axial at C-1 and C-5, and equatorial at C-2 and C-6 is in agreement with data for related compounds,[4,5] based on the coupling constants $J_{1,2} = J_{5,6} = 3{\cdot}5$ Hz. Hence the same stereochemistry can be assigned to (**1**)[5] ($J_{1,2} = J_{5,6} = 3{\cdot}5$ Hz) and (**2**)[7] ($J_{1,2} = J_{5,6} = 2$ Hz). The ^{1}H and ^{13}C n.m.r. and the mass spectral data are in good agreement with a reported epoxy-lactone prepared from a known related compound.[5] From decoupling experiments (Bruker WH-270 instrument), H-2 can now be assigned the signal at δ 5·28 and H-6 at 5·27.



(**4**)

Ar^1 = 3,5-Dimethoxy-4-hydroxyphenyl
Ar^2 = 3-Methoxy-4-hydroxyphenyl

Together with (**3**), a new epoxy-lignanolide from *Aegilops ovata L.* has been isolated and given the structure (**4**), $C_{21}H_{22}O_8$, ν_{max} (KBr) 1775 cm^{-1}; λ_{max} (MeOH) 236 and 290 nm; ^{1}H n.m.r. spectrum (270 MHz, $CDCl_3$) δ 3·27 (1H, m, H-5), 3·47 (1H, dd, *J* 9 and 3·5 Hz, H-1), 3·82 (6H, s, 2 × OMe), 3·84 (3H, s, –OMe), 4·15 (1H, dd, *J* 10 and 4 Hz, H-4), 4·32 (1H, dd *J* 10 and 6 Hz, H-4), 5·27 (1H, br d, *J* 3·5 Hz, H-6), 5·29 (1H, br d, *J* 3·5 Hz, H-2), 6·48 (2H, s,

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† The first naturally occurring lignan containing both an ether and a lactone.

Ar^1-H), and 6·96 (3H, s, Ar^2-H). Irradiation at δ 6·96 caused a narrowing of the signal for H-2 due to collapse of long-range coupling with the Ar^2 protons whereas irradiation at δ 6·48 caused narrowing only at H-6. This suggested that the third OMe group can only be in the Ar^1 ring and mass spectral evidence confirmed the above observations; m/e (M^+) 402 (90%), 193 (22), 167 (100), and 151 (70).

(*Received*, 28*th July* 1977; *Com.* 779.)

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[1] D. Gross, *Phytochemistry*, 1975, **14**, 2105.

[2] C. F. Van Sumere, J. Cottenie, J. de Greef, and J. Kint, *Recent Adv. Phytochemistry*, 1972, **4**, 165.

[3] D. Lavie, E. C. Levy, A. Cohen, M. Evenari, and Y. Gutterman, *Nature*, 1974, **249**, 388.

[4] C. H. Brieskorn and H. Huber, *Tetrahedron Letters*, 1976, 2221.

[5] A. S. Anjaneyulu, A. M. Rao, V. K. Rao, L. R. Row, A. Pelter, and R. S. Ward, *Tetrahedron*, 1977, **33**, 133

[6] W. I. Taylor and A. R. Battersby, 'Oxidative Coupling of Phenols,' Marcel Dekker, New York, 1967.

[7] R. Ahmed, M. Lehrer, and R. Stevenson, *Tetrahedron*, 1973, **29**, 3753.

[8] K. V. Sarkanen and A. F. A. Wallis, *J.C.S. Perkin I*, 1973, 1878.