films unless noted otherwise) were recorded on a Nicolet 20DXB spectrometer. Mass spectra were determined on a Kratos MS 25 spectrometer. Elemental analyses were performed by MicAnal, Tucson, AZ.

Di-*tert*-butyl ketone was synthesized by using the procedure of DuBois and Bauer.[10] A stock soluton of methallylmagnesium chloride in THF was prepared by analogy to the method of Otto and Van Zanten.[11] All other reagents were obtained commercially and used as received. THF was distilled from Na/benzophenone.

General Procedure for Homoallyl Alcohols 3a–e. A 30-mL portion of stock methallyl magnesium chloride solution (0.94 M, in THF) was stirred at 0 °C under an N_2 atmosphere. A solution of ketone **2** (25 mmol) in dry THF (10 mL) was added dropwise over 15 min. The solution was then allowed to stir at 20 °C for 40 min, at which time the reaction was quenched with saturated aqueous NH_4Cl. The organic phase was separated and the aqueous phase extracted with pentane. The combined organics were dried over $MgSO_4$, filtered, and concentrated. The residue was purified by bulb-to-bulb distillation.

Ozonolysis: Preparation of β-Ketols 4a–e. A solution of homoallylic alcohol **3** (24 mmol) in CH_2Cl_2 (30 mL) was cooled to −70 °C. Ozone was bubbled through the solution until a blue color developed. After 5 min, the excess ozone was removed with an O_2 purge, and dimethyl sulfide (30 mmol) was added. The solution was allowed to warm to 20 °C and stirred for 8 h. The solvent was removed under vacuum, and the residue partitioned between pentane and saturated brine. The organic phase was dried, filtered, and concentrated to give the crude ketol **4**, which was generally not purified further.

Dehydration: Enones 5a,b,d,e. Ketol **4** (3.2 g) was combined with oxalic acid (3.2 g) and 50 mL of water. The mixture was heated at reflux for 30 min and then distilled until no more organic material came over. The distillate was extracted with pentane (3 × 10 mL). The extracts were dried over $MgSO_4$, filtered, and concentrated. The crude material was purified by bulb-to-bulb distillation.

4-*tert*-Butyl-2,5,5-trimethyl-4-[(4-nitrobenzoyl)oxy]hex-1-ene (6). The ester, prepared from alcohol **3c** by the procedure of Kaiser and Woodruff,[10] was obtained as pale yellow needles from methanol (77%): mp 97.5–98.5 °C; IR (KBr) ν 1708, 1525, 1280, 890 cm^{-1}; ^1H NMR δ 8.26 (m, 4 H), 4.84 (m, 2 H), 3.30 (br s, 2 H), 1.70 (br s, 3 H), 1.30 (s, 18 H). Anal. Calcd for $C_{20}H_{29}O_4$: C, 69.14; H, 8.41; N, 4.03. Found: C, 69.35; H, 8.41; N, 4.10.

4-*tert*-Butyl-5,5-dimethyl-4-[(4-nitrobenzoyl)oxy]hexan-2-one (7). A solution of ene ester **6** in CH_2Cl_2 was ozonized as above. The crude product was purified by column chromatography (CH_2Cl_2 eluent), followed by crystallization from methanol, to provide white needles of **7** (45%): mp 121.5–122 °C; IR (KBr) ν 1730, 1719, 1523, 1285 cm^{-1}; ^{1}HNMR δ 8.23 (m, 4 H), 3.51 (s, 2 H), 2.20 (s, 3 H), 1.23 (s, 18 H). Anal. Calcd for $C_{19}H_{27}NO_5$: C, 65.31; H, 7.79; M, 4.01. Found: C, 64.99; H, 7.82; N, 3.94.

4-*tert*-Butyl-5,5-dimethyl-3-hexen-2-one (5c). A solution of keto ester **7** (27.8 mg) in benzene (1 mL) and DBU (50 mg) was heated at 80 °C for 2.5 hours. The yellow mixture was diluted with 2 mL of benzene and washed with 0.3 M H_2SO_4 (5 mL). The organic phase was filtered through $MgSO_4$ and concentrated. Pure enone was obtained by bulb-to-bulb distillation [97 °C (20mm)] yielding 13.5 mg (91%) of **5c**: see Table II.

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Registry No. **2a**, 75-97-8; **2b**, 565-80-0; **2c**, 815-24-7; **2d**, 120-92-3; **2e**, 76-22-2; **3a**, 107035-96-1; **3b**, 107035-97-2; **3c**, 107035-98-3; **3d**, 67570-15-4; **3e**, 107035-99-4; **4a**, 42095-30-7; **4b**, 107036-00-0; **4c**, 107036-01-1; **4d**, 38134-31-5; **4e**, 107036-02-2; **5a**, 23732-21-0; **5b** (isomer 1), 107036-03-3; **5b** (isomer 2), 107036-04-4; **5c**, 107036-05-5; **5d** (isomer 1), 933-02-8; **5d** (isomer 2), 823-91-6; **5e**, 107036-06-6; **6**, 106140-00-5; **7**, 106140-07-2; 4-$NO_2C_6H_4COCl$, 122-04-3; methallylmagensium chloride, 5674-01-1; acetone enolate, 71695-00-6.

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Structural Elucidation of a Novel Deoxynivalenol Analogue

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Deoxynivalenol (3α,7α,15-trihydroxy-12,13-epoxytrichothec-9-en-8-one, vomitoxin) is one of the predominant trichothecene mycotoxins associated with infection of cereal grains by certain *Fusarium* species[1] and is cause for concern from the viewpoint of both animal and human health.[2]

Recently, a number of studies[3] have focused on the fate of deoxynivalenol during food processing. In a baking study[4] with contaminated flour, we reported the conversion of deoxynivalenol to a diosphenol isomer. This isomer was identified by comparison of its spectral characteristics with an acetylated analogue formed during acetylation studies with deoxynivalenol. While pursuing synthetic studies aimed at a large-scale preparation of the diosphenol isomer, we isolated a new oxidative analogue of deoxynivalenol. In this paper, we report the preparation and structural elucidation of the new compound.

Results and Discussion

As reported previously,[4] when deoxynivalenol (**1**) is refluxed vigorously with acetic anhydride, it is converted in high yield to the triacetylated diosphenol (**2**) (Scheme I). Workup of the reaction involves neutralization with aqueous sodium bicarbonate prior to extraction with chloroform and preparative thin-layer chromatography of the chloroform residue. When a large-scale batch from the described reaction was subjected to preparative thin-layer chromatography, the presence of a slightly more mobile (than compound **2**) pale yellow component became apparent. Extraction and crystallization of this component furnished pale yellow homogeneous crystals with physical and spectral properties that did not correlate with those of any previously reported derivative of deoxynivalenol (**1**). Molecular weight data for the compound determined by fast atom bombardment mass spectrometry was 378 (MH^+ at m/z 379), 2 mass units less than that of 3,15-diacetoxydeoxynivalenol. Its infrared spectrum revealed the presence of four carbonyl groups and absorption in the ultraviolet showed a strong maximum at 248 nm, indicating that the α,β-enone system was still intact. The ^1H NMR spectrum (Table I) confirmed loss of the C-7 proton, and a downfield shift of H-11 suggested greater polarization of the conjugated α,β-enone system. In its ^{13}C NMR spectrum (Table I), the normal C-7 absorption (ca. 70 ppm)

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Scheme I

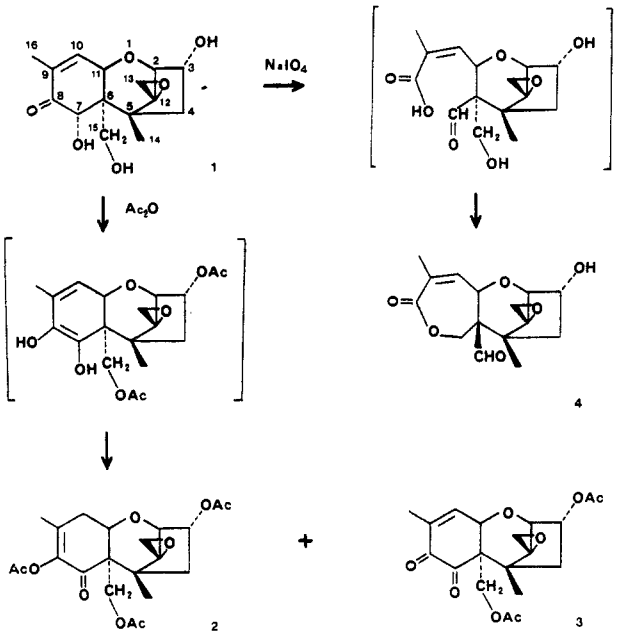

Table I. ^1H and ^{13}C NMR Assignments for Compound 3

carbon no.	δ(H)	δ(C)
2	3.83 (d, 1 H, J = 4.5 Hz)	78.9 (1)[a]
3	5.27 (m, 1 H)	70.6 (1)
4	2.25 (ABX, 2 H)	40.1 (2)
5		45.3 (0)
6		59.2 (0)
7		182.7 (0)
8		194.0 (0)
9		141.1 (0)
10	6.94 (dd, 1 H, J = 6.0, 1.6 Hz)	141.5 (1)
11	4.74 (d, 1 H, J = 6.0 Hz)	70.4 (1)
12		64.7 (0)
13	3.01, 3.26 (AB, 2 H)	50.3 (2)
14	1.20 (s, 3 H)	13.3 (3)
15	4.35 (AB, 2 H, J = 11.8 Hz)	64.7 (2)
16	1.99 (s, 3 H)	15.3 (3)
CH_3 (Ac)	1.96 (s, 3 H)	20.4 (3)
CH_3 (Ac)	2.15 (s, 3 H)	20.7 (3)
C=O		170.1 (0)
C=O		170.06 (0)

[a] Multiplicity (number of directly attached protons).

for nivalenol-type trichothecenes has been replaced by another signal of zero multiplicity at 183 ppm. Such a signal is characteristic of a ring carbonyl group. On the basis of these properties, the new deoxynivalenol analogue was assigned the unique diketo structure **3**.

The formation of **3** most likely originates via oxidation of an assumed enediol intermediate,[4] since earlier efforts at selective oxidation of the 7α-hydroxy-8-keto system in deoxynivalenol (for chemical confirmatory purposes)[5] yielded only the seven-membered lactone structure **4**. The formation of this lactone was rationalized by assuming initial oxidative cleavage at C-7,C-8 to yield a C-7 aldehyde and a C-8 carboxylic acid, respectively. Subsequent or concerted esterification of the C-15 hydroxyl with the C-8 carboxylic acid would lead to the lactone isolated.

Experimental Section

Melting points were determined on a Kofler hot-stage microscope and are uncorrected. IR spectra were determined by using a Beckman IR-20A spectrophotometer. NMR spectra were obtained in $CDCl_3$ solution with Me_4Si as an internal standard on a Bruker WM 250 NMR spectrophotometer at 250 and 62.8 MHz. FAB-MS were recorded on a Finnigan MAT 312 mass spectrometer. Ultraviolet spectra were determined on a Perkin-Elmer Model LC-85 spectrophotometric detector. Thin-layer chromatograms were run on glass plates coated with silica gel GF (layer thickness 0.5 mm). Separated components were detected by ultraviolet fluorescence and (or) by charring after a spray of 5% sulfuric acid in ethanol.

Reaction of Deoxynivalenol (1) with Acetic Anhydride. Deoxynivalenol (**1**; 500 mg) was refluxed in acetic anhydride (40 mL) with stirring, until TLC studies indicated that transformation was completed (ca. 1.8 h). The reaction mixture was then cooled and neutralized by decantation into a cold saturated solution of sodium bicarbonate (100 mL). The neutral solution was extracted with chloroform (2 × 100 mL), and the extracts were concentrated under vacuum. The residue was then purified by preparative TLC on silica gel plates developed with ethyl acetate–hexane (1:1). The major component, 3,8,15-triacetoxy-12,13-epoxytrichothec-8-en-7-one (**2**; 374 mg), at R_f 0.47 was purified by recrystallization from ethanol and its identity confirmed by comparison with a specimen characterized previously.[4] A minor compound with R_f 0.59 (21 mg) was also crystallized from ethanol and furnished 3,15-diacetoxy-12,13-epoxytrichothec-9-ene-7,8-dione (**3**) as pale yellow needles: mp 158–159 °C; IR (Nujol) 1746, 1738, 1698, 1690 cm^{-1}; UV ($CHCl_3$) λ_{max} 248 nm; ^1H NMR and ^{13}C NMR spectral data in Table I; MS (FAB) m/z 378.2 (M^+). Attempted deacetylation with either sodium ethoxide or methanolic ammonia degraded the compound.

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The Dechloroaridicin Antibiotics: Preparation and Characterization

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The aridicins are a series of complex glycopeptide antibiotics related to the vancomycin–ristocetin family[1] and produced by a new genus, *Kibdelosporangium aridum* (ATCC 39323).[2,3] Three major antibiotics, i.e., aridicin A–C have been isolated and their structures recently determined.[4] Their biosynthetic origins have also been studied.[5,6] These antibiotics share an identical aglycone structure and differ only in the size of the *N*-acyl side chain of the 2-amino-2-deoxyglucopyranuronic acid moiety.

The glycopeptide antibiotics of this class have been subjects of current interest because of the increasing clinical role of vancomycin for treatment of methicillin-resistant staphylococcal infections. They are believed to exert their antibacterial activity by interfering with cell-wall biosynthesis presumably through a strong binding to the cell-wall precursors terminating with L-Lys-D-Ala-D-Ala.[1] The interactions of glycopeptides with a model tripeptide, Ac_2-L-Lys-D-Ala-D-Ala have been recent topics of several elegant NMR studies.[7-11] According to these model studies, the tripeptide is bound to the glycopeptide antibiotics by several hydrogen-bonding interactions in-

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