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TRITICONES, SPIROCYCLIC LACTAMS FROM THE FUNGAL PLANT PATHOGEN *DRECHSLERA TRITICI-REPENTIS*

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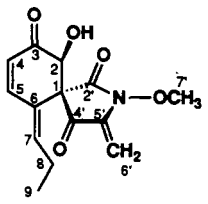
ABSTRACT.—Triticones A [**1**], B [**2**], C [**3**], D [**4**], E [**5**], and F [**6**] were isolated from the culture broth of the plant pathogenic fungus *Drechslera tritici-repentis* (=*Pyrenophoria tritici-repentis*). The structures of these γ-lactams were determined by a combination of single crystal X-ray diffraction and spectroscopic analyses. A series of 2D nmr experiments has clarified the spectral assignments of triticones A [**1**] and B [**2**] and their interconversion.

Fungi that attack plants, fungal pathogens, chemically infect their host plants by secreting phytotoxic secondary metabolites (1). These phytotoxins play a crucial role in causing the various symptoms associated with fungal-induced plant diseases (2) and are also an underexplored source of chemically new and potentially useful compounds (3). We are exploring the possibility of characterizing novel phytotoxins from fungi that attack weeds and using these structures as leads for new herbicides (3). Our initial communication dealt with triticones A [**1**] and B [**2**], their characterization by single crystal X-ray diffraction, and their interconversion (4). In addition to giving more details on triticones A [**1**] and B [**2**], we report the isolation and characterization of triticones C [**3**], D [**4**], E [**5**], and F [**6**].



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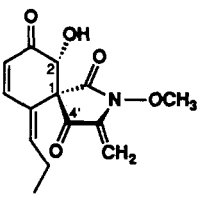

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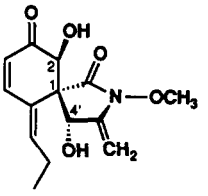

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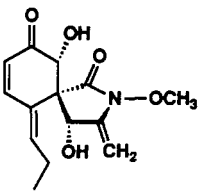

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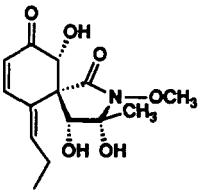

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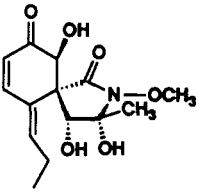

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RESULTS AND DISCUSSION

Drechslera tritici-repentis (Diedieke) Shoemaker (=*Pyrenophoria trichostoma*, perfect stage) attacks weeds such as crested wheat grass, *Agropyron cristatum* Gaertner. (Gramineae) and quackgrass, *Agropyron repens* L. (Gramineae) (4) along with commercially important crops such as wheat [*Triticum vulgare* L. (Gramineae)] and rye [*Secale cereale* L. (Gramineae)]. *D. tritici-repentis* was cultured on a modified M-1-D medium (5), and three-week-old cultures were extracted with EtOAc. The extracts were fractionated with Si gel (6) and Sephadex LH-20 chromatography to give the various compounds discussed below. The biological activity was assessed by the leaf puncture method (7), which gave yellowish-brown spots for active compounds when 2-μl drops of 10^{-5} mol solutions were applied.

TRITICONES A [**1**] AND B [**2**].—The most active compounds were triticones A [**1**] and B [**2**], which were produced in an approximately 1:1 ratio at a combined level of 12 mg/liter of culture broth. While we have never been able to separate the mixture of triticones A and B, slow evaporation of an EtOAc solution in the cold gave crystals suitable for X-ray analysis (4). The crystals belonged to space group $P2_12_12_1$ ($Z=8$) with $a=9.026$ (2), $b=13.387$ (3), and $c=23.214$ (4) Å, and the details of the X-ray analysis are given in the Experimental section. A drawing of the final X-ray model is shown in Figure 1. The molecule defined by the X-ray analysis was called triticone A [**1**] and there were two independent molecules in the asymmetric unit. The two independent molecules were related as enantiomers, i.e., a racemic mixture of **1** crystallized from solution. The optical rotations of freshly isolated triticones A and B were typically small, $[\alpha]^{25}D$ varied from 0° to −9°, and dependent on the sample's history. Nmr spectra also indicated curious behavior for the triticones A and B. Both the ^1H- and ^{13}C-nmr spectra showed that, in solution, the active fraction was a mixture of two closely related compounds in the approximate ratio of 10:9. We tentatively assumed that the major component was the form that crystallized, triticone A [**1**], and called the additional solution component triticone B [**2**]. The correctness of this assumption as well as the stereochemistry of triticone B [**2**] was determined spectroscopically.

The X-ray analysis clearly shows that triticone A [**1**] is a racemate in the solid state and has the hydroxyl group at C-2 in a pseudoequatorial conformation. However, 2D

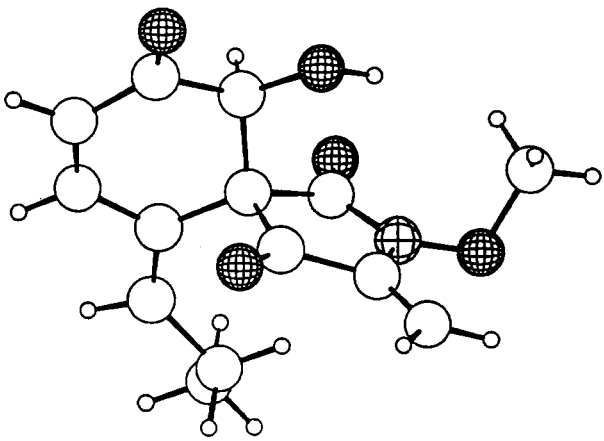
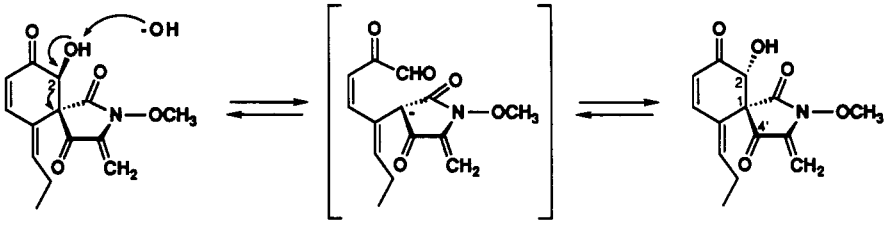


FIGURE 1. A computer generated perspective drawing of the final X-ray model of triticone A [**1**]. No absolute configuration is implied (see text).

^{1}H-^{1}H shift correlation spectroscopy (2D COSY) showed two different conformations of the C-2 hydroxyl to be present in solution. Both the methine and hydroxyl protons on C-2 exhibited cross peaks at δ 4.62 and 3.84 for major isomer **1** and δ 4.72 and 3.70 for minor isomer **2**. Other peaks showed similar behavior. For example, the cross peaks of the exomethylene protons on C-6′ were observed at δ 5.38 and 4.92 for major isomer **1** and δ 5.25 and 4.89 for minor isomer **2**. The ^{1}H-nmr spectrum was assigned with ^{1}H-^{1}H spin decoupling and ^{1}H-^{1}H COSY experiments as described in the Experimental section. In making these assignments, it was assumed that the stronger peaks could be attributed to **1** and the weaker peaks to **2**.

The relative stereochemistry of **2** was deduced from nOe experiments (2D NOESY) (8,9). In isomer **2**, the exomethylene proton on C-6′ at δ 4.91 showed a cross peak with the C-2 proton at δ 4.72. In isomer **1**, there was no nOe observed for the C-2 and C-6′ protons. If **1** were the structure revealed in the X-ray analysis, this is precisely the expected result: no nOe between C-2 and C-6′ protons. If **2** were the C-2 epimer of **1**, nOe correlation between the proton on C-2 and a proton on C-6′ would be expected. The 2D NOESY also showed that the cross peaks between forms **1** and **2** originated in the epimerization at C-2. The cross peaks for the exomethylene protons (C-6′) were observed at δ 5.38 in **1** and δ 5.25 in **2**. The cross peaks for the methine proton at δ 4.62 (**1**) and 4.72 (**2**) and hydroxyl proton at δ 3.84 (**1**) and 3.70 (**2**) were also recorded.

Finally, there is an economical mechanistic path which interconverts and racemizes triticones A [**1**] and B [**2**] through the achiral intermediate shown in Scheme 1. The scheme is illustrated with a hydroxide catalyst for simplicity; other bases could work as well or essentially the same chemistry could be accomplished with acidic catalysts. In the retro-Aldol type reaction shown, this molecule would be converted to an intermediate anion in which both of the sp^3-hybridized chiral centers have been rehybridized to planar sp^2 achiral centers. The reverse reaction to reform **1** would, in the absence of a chiral environment, give **1** in racemic form. Alternatively, the intermediate anion could cyclize in a different sense to give **2** and its enantiomer with equal probability. Scheme 1 provides a plausible explanation for both optical activity and nmr behavior of the sample.



SCHEME 1

TRITICONE C [**3**].—Triticone C [**3**] was obtained as pale yellow oil in a yield of 16 mg/liter of culture fluid. The molecular formula, determined by hreims, was $C_{14}H_{17}N_1O_5$, suggesting that triticone C might be generated by adding two hydrogens to triticones A [**1**] and B [**2**]. The speculation was completely supported by both the ^{1}H- and ^{13}C-nmr spectra, which were very similar to those of the triticone A and B mixture. The relative simplicity of the nmr spectra of triticone C [**3**] showed that it was a single compound, not an interconverting mixture of compounds. The ^{1}H nmr

of **3** showed two additional signals, one at δ 4.65 and the other at δ 1.92. These signals were coupled to each other (6.6 Hz). The signal at δ 1.92 disappeared upon addition of D_2O as did the signal at δ 3.74 which had been assigned to the C-2 hydroxyl. The signal at δ 4.65 was coupled with the exomethylene protons at C-6′ (δ 4.75 and 4.57) with a coupling constant of 1.7 Hz, which indicated an allylic coupling. In the ^{13}C-nmr spectrum, one of carbonyl carbons (C-4′) at δ 191.6 of **1** was replaced by a hydroxylated carbon at δ 64.5 in triticone C [**3**]. Clearly one of the carbonyls of **1** had been reduced to an alcohol, and the coupling with the C-6′ protons indicated that C-4′ was the only possible choice.

The stereochemistry shown in the structure **3** for triticone C was determined by nmr spectroscopy. In the ^1H nmr, no nOe's between the protons on C-2, C-4′, and C-6′ were observed by 1D differential experiments. The absence of an nOe between H-4′ and H-8 indicated that the proton on C-4′ was not located on the same face of the lactam ring as the C-8 methylene protons. Thus the stereochemistry at C-4′ was α hydroxyl and β proton as shown in **3**. The absence of an nOe between the proton at C-2 and that at C-4′ indicated that they were on opposite faces of the cyclohexenone ring. The relative stereochemistry shown in **3** was determined by missing nOe's, but the structural assignment was strengthened by the single crystal X-ray analysis of triticone D [**4**] described below.

TRITICONE D [**4**].—The fourth compound isolated, triticone D, was isolated in a yield of 6 mg/liter and had the same molecular formula ($C_{14}H_{17}N_1O_5$) as triticone C [**3**] from hreims. This compound crystallized from cold EtOAc and was analyzed by single crystal X-ray diffraction. Crystals formed in the orthorhombic space group $P2_12_12_1$ with $a = 8.375\,(4)$, $b = 6.499\,(3)$, and $c = 24.850\,(11)$ Å, and the final crystallographic discrepancy index was 0.050 for the 972 observed reflections. A computer-generated perspective drawing of the final X-ray model is given in Figure 2. Triticone D [**4**], like triticone C [**3**], had the C-4′ carbonyl reduced to a hydroxyl, and the

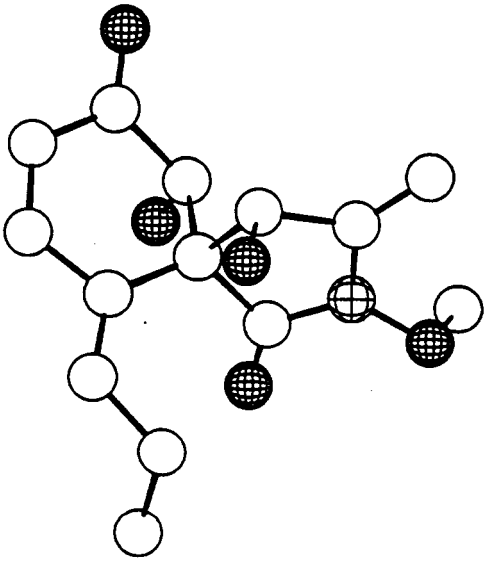


FIGURE 2. A computer generated perspective drawing of the final X-ray model of triticone D [**4**]. No absolute configuration is implied (see text).

stereochemistry at C-4′ had the hydroxyl in α configuration or on the same face as the C-8 methylene. Triticones D and C differed in their stereochemistry at C-2. In triticone D [**4**], the proton on C-2 was on the same face of the cyclohexenone ring as the proton on C-4′.

Finally it should be noted that both triticones C [**3**] and D [**4**] did not show the rapid interconversion that characterized the A and B mixture. Presumably the anionic intermediate shown in Scheme 1 needs both carbonyl groups to stabilize it and to make the interconversion facile.

TRITICONES E [**5**] AND F [**6**].—These two compounds were not separable on any chromatographic system we employed; they invariably were a single spot on every tlc system. We were also not able to separate them using a variety of normal and reversed-phase chromatography systems including hplc. Repeated attempts to grow crystals through selective crystallization of one of the components were unsuccessful. The molecular formula of both components was $C_{14}H_{19}N_1O_6$ from hreims, ^1H nmr, and ^{13}C nmr. The molecular formula indicated that triticones E and F were further reduced members of the triticone family. The ^1H-nmr spectrum indicated that the two components were present in a 10:9 ratio, essentially the same ratio obtained for the triticones A and B mixture. The major component was named triticone E, and the minor, F. A significant observation in the ^1H nmr was the absence of exomethylene signals at C-6′ and the appearance of a new methyl and hydroxyl signal indicating that the C-5′–C-6′ double bond had been reduced. Some parts of the ^1H nmr were easy to assign. The paired signals at δ 5.95 and 5.91 (d, $J=9.9$ Hz); δ 7.08 and 7.04 (d, $J=9.9$ Hz); and δ 6.35 and 6.17 (t, $J=7.5$ Hz) were tentatively assigned to the three conjugated olefinic protons at C-4, C-5, and C-7 of the two isomers, respectively. Examination of the COSY spectrum confirmed these assignments. The COSY spectrum allowed us to make a full assignment of the ^1H nmr of both triticones E [**5**] and F [**6**].

NOESY experiments were employed to determine the relative stereochemistries shown in **5** and **6** for both compounds at C-2, C-4′, and C-5′. In the minor component, **6**, the signal for H-6′ was correlated with H-7′ and H-4′. The H-6′–H-4′ correlation indicated that the methyl at C-5′ was on the face opposite the C-4′ hydroxyl. There was no correlation of the protons at C-6′ with the C-2 proton, indicating that C-6′ and the hydroxyl at C-2 were on the same face of the cyclohexenone ring. For the major component, **5**, there was again a correlation of the C-6′ protons with the C-4′ proton, indicating that the C-4′ and C-5′ stereochemistries in **5** were the same as in **6**. However, there was a correlation of the C-6′ protons with the C-2 proton, requiring the opposite stereochemistry at C-2, as shown in Figure 3. The general theme seems to be pairs of compounds, **1–2**, **3–4**, and **5–6**, related as epimers at C-2.

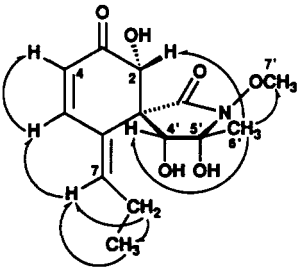


FIGURE 3. Partial identifications of 2D NOESY of **5**. Cross peaks originated by nOe are expressed by arrows.

We made some attempts to assess whether **5** and **6** were rapidly interconverting as a possible explanation of our failure to separate them. Qualitatively we observed that the **5** and **6** mixture was more thermally stable than the **1** and **2** mixture. When triticones E [**5**] and F [**6**] were heated to 70°, both components of the mixture remained unchanged as did the ratio between them. The **5** and **6** mixture had a relatively large, negative and constant optical rotation, unlike the **1** and **2** mixture. Once again, an attractive rationale for this behavior is that the retro-Aldol opening shown in Scheme 1 is less favorable in this case because of the lack of the carbonyl group at C-4′. However, the NOESY spectrum did not rule out the possibility of a slow interconversion of diastereoisomers.

In the leaf protoplast assays, the mixture of A and B is the most phytotoxic of the triticones, C and D showed weak activity, and E and F were essentially inactive (10). The triticones are members of an emerging new class of fungal metabolites. They are structurally very similar to the spirostaphylotrichins isolated recently from *Staphylotrichum coccosporum* (11–13) and arthropsolide A from *Arthropsis truncata* (14). The biosynthetic origin of the compounds produced by *S. coccosporum* has been investigated, and it has been proposed that condensation of a C_{10}-polyketide precursor and aspartate followed by cyclization is involved in the formation of the general skeleton (15). Triticones are highly functionalized fungal metabolites, and our efforts to explore their chemistry and biological activity are continuing.

EXPERIMENTAL

INSTRUMENTS.—Nmr spectra were recorded on JEOL JNM GX400 and Varian XL-400 spectrometers. Chemical shifts were expressed by δ units in ppm from TMS as internal standard. Ir spectra were recorded on a Shimadzu IR-435 spectrometer. Uv spectra were obtained from Hitachi 225A spectrophotometer. Ms was recorded on a Hitachi M-80 instrument. Optical rotations were determined with Perkin-Elmer Model 241 MC polarimeter. Cc absorbents include Si gel 60 (230–400 mesh, E. Merck, Darmstadt) and Sephadex LH-20 (Pharmacia Fine chemicals, Uppsala, Sweden). The hplc columns employed were Lichrosorb RP-18 (4 × 250 mm, E. Merck) and Senshu-Pak ODS-H-3151 (8 × 150 mm, Senshu, Tokyo, Japan).

CULTURE BROTH AND PLANT ASSAY.—Freeze-dried cultures of *D. tritici-repentis* were obtained from the mycological collection of the Department of Plant Pathology, Montana State University, and were maintained on potato dextrose agar plates (Difco Laboratories, NJ) containing V-8 juice (18% by volume). The fungus used for toxin production was grown at 26° in 2-liter Erlenmeyer flasks containing 1 liter of modified M-1-D medium. The medium was adjusted to pH 5.5 with 0.1 N HCl, sterilized by autoclaving, and then inoculated by mycelium from a culture plate. Cultures were shaken at 200 rpm at 26° for 3 weeks under luminescence in an incubator. Seeds of wheat, *Triticum aestivum* L. (Gramineae), lambsquarters, *Chenopodium album* L. (Chenopodiaceae), redspot pigweed, *Amaranthus retroflexus* L. (Amaranthaceae), and dandelion, *Taraxacum officinale* Wigg. (Compositae) were planted in plastic pots containing Batco potting soil (Michigan Peat Co.) and grown in an environmentally controlled greenhouse at 22–24° on the campus of Montana State University. The plants used for assay were 2–4 weeks old after germination. A droplet (1–5 μl) of a 2% EtOH solution containing 10^{-7}–10^{-3} mol concentration of components was placed on a leaf blade over a puncture wound to enhance access to the leaf tissue. The leaves were placed on moist filter paper in a sealed Petri dish at 28° for 48 h under light. The phytotoxic effects were observed as yellowish-brown lesions and no symptoms were observed with 2% EtOH control solvent.

EXTRACTION AND PURIFICATION.—The fungal mycelia were removed from the culture broth by filtration with a four-layer cheesecloth filter. The filtrate was extracted with EtOAc, and all of the phytotoxic activity was found in the organic phase. The organic fraction was washed with H_2O and evaporated under reduced pressure below 30° to give an oily residue (140 mg). The residue was further purified, guided by plant assay, by using several successive flash Si gel columns eluted with $CHCl_3$-MeOH (14:1) or toluene-EtOAc (1:1). Triticones were obtained following chromatography on Sephadex LH-20 eluted with MeOH. R_f values on tlc were determined on precoated Kiesel Gel 60 F_{254} plates (5 × 10 cm, E. Merck) in $CHCl_3$-MeOH (14:1) (solvent system A) and toluene-EtOAc (1:1) (solvent system B). Compounds were visualized on tlc plates with anisaldehyde/H_2SO_4/HOAc reagent in MeOH and were visable by uv absorbance at 254 nm.

Triticones A [**1**] *and B* [**2**].—Colorless crystals from EtOAc: yield 12.0 mg/liter; mp 42–45° (dec); $[\alpha]^{25}D$ 0° to −9° (c = 1.0, $CHCl_3$); R_f 0.63 (solvent A) and 0.52 (solvent B); uv λ max (EtOH) nm (log ε) 288 (4.08), 208 (4.11); ir ν max (KBr) cm^{-1} 3460, 2970, 1760, 1725, 1690, 1680, 1620, 1585, 1440, 1380, 1280, 1100; eims *m/z* (rel. int.) 277 (100), 246 (35), 220 (21), 218 (50), 200 (16), 190 (25), 188 (24), 121 (29); hreims *m/z* $[M]^+$ 277.0945 ($C_{14}H_{15}NO_5$) (calcd 277.0950); ^1H nmr (400 MHz, $CDCl_3$) for **1** δ 7.04 (d, 1H, J = 10.0 Hz, H-5), 6.09 (d, 1H, J = 10.0 Hz, H-4), 6.06 (t, 1H, J = 7.3 Hz, H-7), 5.38 (d, 1H, J = 2.1 Hz, H_a-6′), 4.92 (d, 1H, J = 2.1 Hz, H_b-6′), 4.62 (d, 1H, J = 2.1 Hz, H-2), 4.04 (s, 3H, H-7′), 3.84 (d, 1H, J = 2.1 Hz, OH), 2.18–1.90 (m, 2H, H-8), 0.97 (t, 3H, J = 7.4 Hz, H-9); for **2** δ 7.05 (d, 1H, J = 9.7 Hz, H-5), 6.07 (d, 1H, J = 9.7 Hz, H-4), 6.06 (t, 1H, J = 7.3 Hz, H-7), 5.25 (d, 1H, J = 2.1 Hz, H_a-6′), 4.89 (d, 1H, J = 2.1 Hz, H_b-6′), 4.72 (d, 1H, J = 2.1 Hz, H-2), 3.94 (s, 3H, H-7′), 3.70 (d, 1H, J = 2.1 Hz, OH), 2.18–1.90 (m, 2H, H-8), 1.01 (t, 3H, J = 7.3 Hz, H-9); ^{13}C nmr (100 MHz, $CDCl_3$) for **1** δ 194.3 (s, C-3), 191.6 (s, C-4′), 164.6 (s, C-2′), 149.9 (d, C-5), 146.8 (d, C-7), 137.5 (s, C-5′), 127.0 (s, C-6), 121.2 (d, C-4), 91.6 (t, C-6′), 72.7 (d, C-2), 62.6 (q, C-7′), 60.0 (s, C-1), 22.2 (t, C-8), 12.2 (q, C-9); for **2** δ 194.1 (s, C-3), 189.8 (s, C-4′), 162.7 (s, C-2′), 149.4 (d, C-5), 147.2 (d, C-7), 136.6 (s, C-5′), 128.2 (s, C-6), 121.0 (d, C-4), 91.5 (t, C-6′), 73.2 (d, C-2), 62.6 (q, C-7′), 60.2 (s, C-1), 17.6 (t, C-8), 12.8 (q, C-9).

Triticone C [**3**].—Pale yellow oil: yield 16.0 mg/liter; $[\alpha]^{25}D$ +2.0° (c = 1.0, $CHCl_3$); R_f 0.38 (solvent A) and 0.14 (solvent B); uv λ max (EtOH) nm (log ε) 228 (3.92), 222 (4.04); ir ν max (film) cm^{-1} 3450, 2900, 1720, 1685, 1760, 1650, 1620, 1580, 1440, 1370, 1260, 1100; eims *m/z* (rel. int.) 279 (68), 248 (14), 230 (24), 204 (25), 177 (100), 161 (97), 133 (43), 105 (49); hreims *m/z* $[M]^+$ 279.1097 ($C_{14}H_{17}NO_5$) (calcd 279.1106); ^1H nmr (400 MHz, $CDCl_3$) δ 7.07 (d, 1H, J = 10.0 Hz, H-5), 6.29 (t, 1H, J = 7.6 Hz, H-7), 5.98 (d, 1H, J = 10.0 Hz, H-4), 4.79 (d, 1H, J = 2.0 Hz, H-2), 4.75 (dd, 1H, J = 1.7, 1.7 Hz, H-6′), 4.65 (dd, 1H, J = 1.7, 6.6 Hz, H-4′), 4.57 (dd, 1H, J = 1.7, 7.7 Hz, H-6′), 3.94 (s, 3H, H-7′), 3.74 (d, 1H, J = 2.0 Hz, OH), 2.23 (ddd, 1H, J = 7.3, 7.6, 16.4 Hz, H-8), 2.03 (ddd, 1H, J = 7.3, 7.6, 10.4 Hz, H-8), 1.92 (d, 1H, J = 6.6 Hz, OH), 1.06 (t, 3H, J = 7.3 Hz, H-9); ^{13}C nmr (100 MHz, $CDCl_3$) δ 196.8 (s, C-3), 167.2 (s, C-2′), 152.2 (d, C-7), 151.0 (d, C-5), 143.5 (s, C-5′), 127.9 (s, C-6), 120.4 (d, C-4), 86.3 (t, C-6′), 73.5 (d, C-2), 64.5 (d, C-4′), 62.1 (q, C-7′), 56.9 (s, C-1), 22.9 (t, C-8), 13.2 (q, C-9).

Triticone D [**4**].—Colorless crystals: yield 6 mg/liter; $[\alpha]^{25}D$ +22.0° (c = 0.64, MeOH); R_f 0.38 (solvent A) and 0.14 (solvent B); uv λ max (EtOH) nm (log ε) 290 (4.40), 226 (4.51); ir ν max (film) cm^{-1} 3470, 2960, 2920, 1715, 1665, 1652, 1602, 1348, 1231; eims *m/z* (rel. int.) 279 (68), 251 (13), 248 (14), 230 (24), 204 (25), 202 (20), 177 (100), 161 (97), 133 (43), 105 (49); hreims *m/z* $[M]^+$ 279.1126 ($C_{14}H_{17}NO_5$) (calcd 279.1106); ^1H nmr (300 MHz, $CDCl_3$) δ 7.04 (d, 1H, J = 10.0 Hz, H-5), 6.25 (t, 1H, J = 7.6 Hz, H-7), 5.94 (d, 1H, J = 10.0 Hz, H-4), 4.75 (s, 1H, H-2), 4.72 (dd, 1H, J = 1.6, 1.8 Hz, H_a-6′), 4.62 (br s, 1H, H-4′), 4.53 (dd, 1H, J = 1.6, 1.6 Hz, H_b-6′), 3.91 (s, 3H, H-7′), 3.71 (br s, 1H, OH), 2.15 (m, 1H, H_a-8), 2.01 (m, 1H, H_b-8), 1.97 (br s, 1H, OH), 1.03 (t, 3H, J = 7.4 Hz, H-9); ^{13}C nmr (100 MHz, $CDCl_3$) δ 196.5 (s, C-3), 167.1 (s, C-2′), 152.1 (d, C-7), 151.3 (d, C-5), 143.5 (s, C-5′), 127.8 (s, C-6), 120.7 (d, C-4), 86.5 (t, C-6′), 73.6 (d, C-2), 64.9 (d, C-4′), 62.3 (q, C-7′), 56.9 (s, C-1), 23.2 (t, C-8), 13.5 (q, C-9).

SINGLE CRYSTAL X-RAY STRUCTURE DETERMINATION OF **4**[2].—Crystals of **4** were grown by slow evaporation of EtOAc in the refrigerator. A single crystal with dimensions 0.1 × 0.1 × 0.2 mm^3 was chosen for the X-ray analysis. Preliminary X-ray photographs displayed orthorhombic symmetry, and accurate lattice constants of a = 8.375 (4), b = 6.499 (3), and c = 24.850 (11) Å were determined from a least-squares fit of 15 diffractometer-measured 2θ values. The crystal density, 1.37 g/cm^3, indicated that four molecules made up the unit cell. Systematic extinctions were consistent with the space group $P2_12_12_1$. All unique diffraction maxima with 2θ<114° were collected on an automated four-circle diffractometer with graphite monochromated CuKα radiation (1.54178 Å) and variable speed 1° ω-scans. Of the 1186 reflections surveyed in this fashion, 972 (89%) were judged observed [$F_o > 3\sigma(F_o)$] after correction for Lorentz, polarization, and background effects. Hydrogen atoms were located on a ΔF-synthesis or induced at calculated positions. The final crystallographic discrepancy index was 0.0505 (R_w = 0.0785) for the observed reflections.

Triticone E [**5**] *and Triticone F* [**6**].—Pale yellow oil: yield 18 mg/liter; $[\alpha]^{25}D$ −70° (c = 1.0, MeOH); R_f 0.22 (solvent A) and 0.07 (solvent B); uv λ max (EtOH) nm (log ε) 290 (4.01), 206 (3.89); ir ν max

[2]Atomic coordinates for compound **4** have been deposited at the Cambridge Crystallographic Data Centre and can be obtained on request from Dr. Olga Kennard, University Chemical Laboratory, 12 Union Road, Cambridge CB2 1EZ, UK.

($CDCl_3$) cm^{-1} 3440, 1705, 1670, 1602; eims *m/z* (rel. int.) 297 (5), 279 (36), 224 (100), 207 (27), 193 (24), 178 (96), 164 (75), 151 (54), 149 (81); hreims *m/z* $[M]^+$ 297.1214 ($C_{14}H_{19}NO_6$) (calcd 297.1212); ^1H nmr (400 MHz, $CDCl_3$) for **5** δ 7.08 (d, 1H, $J=9.9$ Hz, H-5), 6.35 (t, 1H, $J=7.5$ Hz, H-7), 5.95 (d, 1H, $J=9.9$ Hz, H-4), 4.73 (s, 1H, H-2), 3.99 (s, 3H, H-7′), 3.80 (s, 1H, H-4′), 2.25 (m, 2H, H-8), 1.56 (s, 3H, H-6′), 1.05 (t, 3H, $J=7.3$ Hz, H-9); for **6** δ 7.04 (d, 1H, $J=9.9$ Hz, H-5), 6.17 (t, 1H, $J=7.5$ Hz, H-7), 5.91 (d, 1H, $J=9.9$ Hz, H-4), 4.73 (s, 1H, H-2), 4.07 (s, 1H, H-4′), 3.97 (s, 3H, H-7′), 2.10 (m, 2H, H-8), 1.66 (s, 3H, H-6′), 1.02 (t, 3H, $J=7.1$ Hz, H-9); ^{13}C nmr (100 MHz, $CDCl_3$) for **5** δ 195.2 (s, C-3), 166.5 (s, C-2′), 154.3 (d, C-5), 152.7 (d, C-7), 127.2 (s, C-6), 119.9 (d, C-4), 90.3 (s, C-5′), 73.3 (d, C-2), 73.1 (d, C-4′), 64.7 (q, C-7′), 56.5 (s, C-1), 30.9 (t, C-8), 23.7 (q, C-6′), 13.1 (q, C-9); for **6**: δ 196.9 (s, C-3), 167.4 (s, C-2′), 152.9 (d, C-5), 150.6 (d, C-7), 128.5 (s, C-6), 120.7 (d, C-4), 86.4 (s, C-5′), 73.3 (d, C-2), 73.1 (d, C-4′), 68.6 (q, C-7′), 56.6 (s, C-1), 23.4 (t, C-8), 18.7 (q, C-6′), 13.3 (q, C-9).

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