exceeded the 8 ng/mL solubility in pure water. We strongly suspect the latter.

In conclusion, the results of these studies show that (1) abamectin 8,9-oxide is more stable than abamectin in Petri dishes and on plant leaves, (2) abamectin 8,9-oxide is associated with plant foliage to a greater extent than is abamectin, and (3) abamectin and its 8,9-oxide have equivalent ingestion toxicity for the two-spotted spider mite. Both penetration and stability are probably the determinants of the improved residual activity of the 8,9-oxide over abamectin. At this time, however, it is not possible to determine the relative contributions of these factors to the increased activity of the 8,9-oxide in laboratory bioassays.

ACKNOWLEDGMENT

We thank Drs. Avery Rosegay and Allen Jones (Merck Sharp & Dohme Research Laboratories) for preparing and characterizing the radiolabeled avermectins used in this study. We are also grateful to Nancy Hilton for bringing pertinent references to our attention, Dr. Thomas Capizzi for statistical advice, and Carl Maurer for his patient aid in generating the stability graph.

Registry No. I, 71751-41-2; avermectin B_{1a}, 65195-55-3; avermectin B_{1a} 8,9-epoxide, 98734-60-2.

LITERATURE CITED

Blizzard, T. A.; Mrozik, H.; Fisher, M. H. Chemical Degradation of Avermectin B_1. *Tetrahedron Lett.* **1988**, *29*, 3163–3167.

Brito, R. M.; Stern, V. M.; Sances, F. V. Physiological Response of Cotton Plants to Feeding of Three *Tetranychus* Spider Mite Species. *J. Econ. Entomol.* **1986**, *79*, 1217–1220.

Bull, D. L.; Ivie, G. W.; MacConnell, J. G.; Gruber, V. F.; Ku, C. C.; Arison, B. H.; Stevenson, J. M.; VandenHeuvel, W. J. A. Fate of Avermectin B_1a in Soil and Plants. *J. Agric. Food Chem.* **1984**, *32*, 94–102.

Dybas, R. A. Avermectins: their chemistry and pesticidal activities. In *Human Welfare and the Environment*; Miyamoto, J., Ed.; Pergamon: New York, 1983; pp 83–90.

Dybas, R. A.; Green, A. St. J. Avermectins: their chemistry and pesticidal activity. In *1984 British Crop Protection Conference. Pests and Diseases*; British Crop Protection Council, Croydon, U.K., 1984; pp 947–954.

Dybas, R. A.; Hilton, N. J.; Babu, J. R.; Preiser, F. A.; Dolce, G. J. Novel Second Generation Avermectin Insecticides and Miticides for Crop Protection. *Topics in Industrial Microbiology*; Demain, A., Hunter-Cevera, J., Rossmoore, H., Somuti, G., Eds.; Elsevier: Amsterdam, 1989; Chapter 23, pp 201–210.

Iwata, Y.; MacConnell, J. G.; Flor, J. E.; Putter, I.; Dinoff, T. M. Residues of Avermectin B_1a on and in Citrus Fruits and Foliage. *J. Agric. Food Chem.* **1985**, *33*, 467–471.

Jeppson, L. R.; Keifer, H. H.; Baker, E. W. *Mites Injurious to Economic Plants*; University of California: Riverside, CA, 1975; pp 120ff.

Maynard, M. S.; Gruber, V. F.; Ku, C. C. Distribution and Degradation of Avermectin B_{1a} on Citrus Fruits. *Abstracts of Papers*, 186th National Meeting of the American Chemical Society, Washington, DC; American Chemical Society: Washington, DC, 1983; PEST 100.

McEnroe, W. D. The Control of Water Loss by the Two-Spotted Spider Mite (*Tetranychus telarius*). *Ann. Entomol. Soc. Am.* **1961**, *54*, 883–887.

Mrozik, H. Avermectin Epoxide Derivatives and Method of Use. U.S. Patent 4 530 921, 1985.

Mrozik, H.; Eskola, P.; Reynolds, G. F.; Arison, B. H.; Smith, G. M.; Fisher, M. H. Photoisomers of Avermectins. *J. Org. Chem.* **1988**, *53*, 1820–1823.

Putter, I.; MacConnell, J. G.; Preiser, F. A.; Haidri, A. A.; Ristich, S. S.; Dybas, R. A. Avermectins: novel insecticides, acaricides and nematicides from a soil microorganism. *Experientia* **1981**, 963–964.

Silcox, D.; Holloway, P. J. A simple method for the removal and assessment of foliar deposits of agrochemicals using cellulose acetate film stripping. *Aspects of Applied Biology. 11. Biochemical and Physiological Techniques in Herbicide Research*; The Association of Applied Biologists: Wellesbourne, Warwicks, 1986; pp 13–17. See also preceding and following papers by these authors.

Received for review December 7, 1988. Accepted May 3, 1989.

Synthesis of a 3-Acyl-4-hydroxycyclohex-3-en-1-one

James E. Oliver,*[†] William R. Lusby,[†] and Rolland M. Waters[‡]

Insect Hormone Laboratory, USDA—ARS, Building 467, BARC-East, Beltsville, Maryland 20705, and Insect Chemical Ecology Laboratory, USDA—ARS, Building 001, BARC-West, Beltsville, Maryland 20705

A synthesis of the title compounds from the isomeric 2-acyl-3-hydroxycyclohex-2-en-1-ones 1 has been developed. The 1,3-diketone system of 1 was preserved as its isoxazole derivative **2**, facilitating manipulation of the remaining carbonyl, which in five steps was removed and reintroduced at the adjacent position. The carbonyl of the resulting 5-ketotetrahydrobenzisoxazole **11a** was sensitive to reduction and was protected as a ketal during reductive disassembly of the isoxazole ring.

A number of 2-acyl-3-hydroxycyclohex-2-en-1-ones 1 and 2-acyl-3,6-dihydroxycyclohex-2-en-1-ones **6** in which R is a saturated or unsaturated long-chain hydrocarbon radical are natural products isolated from insects (Lusby et al., 1987; Mudd, 1978, 1981) and plants (Nemoto et al., 1987). In a recent publication we described the synthesis of **6** starting with the 4-ketotetrahydrobenzisox-

[†] Insect Hormone Laboratory.
[‡] Insect Chemical Ecology Laboratory.

This article not subject to U.S. Copyright. Published 1989 by the American Chemical Society

azole **2** (Oliver and Lusby, 1988); **6** had recently been identified as a component of the setal exudate of the hawthorn lace bug, *Corythucha cydoniae* (Fitch) (Lusby et al., 1989). In ongoing work, a compound isomeric to **6** (R = n-$C_{11}H_{23}$) has been partially characterized from the exudate of the andromeda lace bud, *Stephanitis takeyai* (Drake and Maa) (unpublished); further, a biosynthetically related 2,6-dihydroxalkanophenone produced by the same insect has been found to be a potent inhibitor of prostaglandin synthase in two in vitro systems (Jurenka et al., in press). Thus, there is considerable interest in the synthesis and characterization of these and related systems. In addition to the insect-derived compounds, there has been an enormous increase in interest in elaborated derivatives of **1** as agrochemicals, primarily herbicides [for three typical examples from many recent patents, see Arai et al. (1988), Chevron Research Co. (1986), and Knudsen and Michaely (1988)].

The **1** system is readily available from the corresponding cyclohexane-1,3-diones through enol esterification followed by rearrangement (Mudd, 1985). In contrast, the isomeric 3-acyl-4-hydroxycyclohex-3-ene-1-ones **13a** seem to be unreported. Both of these systems are enol forms of acylcyclohexanediones, and we here describe the synthesis of **13a** (R = n-undecyl) from **1**, again employing an isoxazole ring to facilitate 1,3-diketone manipulations. We also describe spectral comparison of the isomers **1** and **13a** and certain properties of their respective isoxazole derivatives **2** and **11a**.

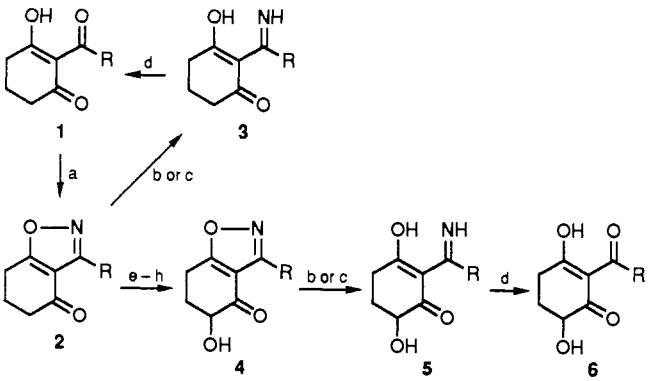
RESULTS AND DISCUSSION

Reduction of **2** (Oliver and Lusby, 1988) to **7** with LAH proceeded without incident (Scheme II). Heating **7** with toluenesulfonic acid in benzene smoothly converted it to olefin **8**. (If the dehydration was interrupted too soon, a dimeric ether (7 + 7 − H_2O) could be isolated. The latter was converted to **8** upon further heating with TsOH.) Disappointingly, hydroboration/oxidation of **8** mainly regenerated **7** (**7**:**10** ≈ 4:1); however, epoxidation followed by LAH reduction of epoxide **9** gave almost exclusively the required **10**. Oxidation of **10** with PCC provided ketone **11a**.

In our work with the 4-keto compounds **2** and **4** (Scheme I), we had determined that hydrogenation with either Pt or Pd catalysts proceeded smoothly when R was saturated to provide imines **3** or **5** (Scheme I). When R contained unsaturation, selective reduction of the isoxazole N–O was achieved by very brief (≤10-s) exposure to $NaBH_4$ in $NiCl_2$-saturated DMF (Oliver and Lusby, 1988). Somewhat surprisingly, that 5-keto analogue **11a** behaved quite differently; it was reduced somewhat more slowly than **2**, and under all of the conditions just mentioned, reduction of the carbonyl, to regenerate alcohol **10**, competed unfavorably with the desired N–O reduction. Somewhat more selective reduction of **11a** to **12a** could be realized with $Mo(CO)_6$ in moist MeCN (Nitta and Kobayashi, 1982) or with$NaBH_4/NiCl_2$ in MeOH, and samples of **12a** were thus obtained. In neither case, however, were recoveries entirely satisfactory.

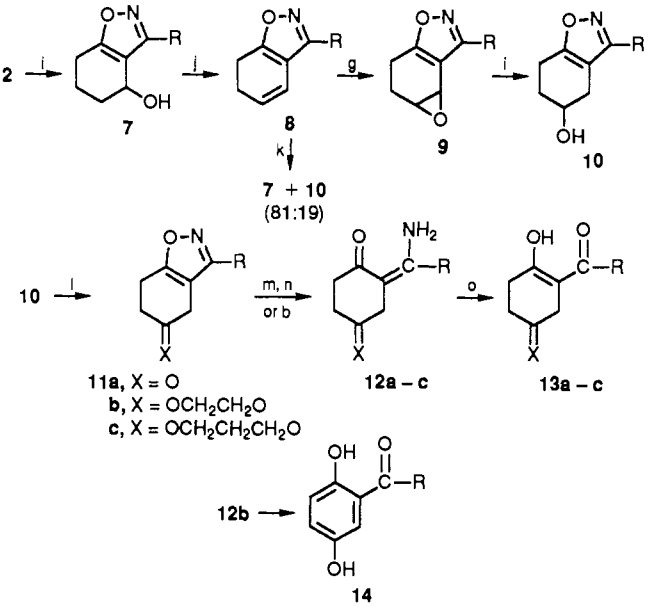
In contrast to simple 3,5-disubstituted isoxazoles, which are reduced to enamino ketones (Wakefield and Wright, 1979), **2** and **4** produced imines **3** and **5** (Oliver and Lusby, 1988); in contrast to enamino ketones, which are easily hydrolyzed by dilute acid, **3** and **5** were stable to aqueous acids but were converted to **1** and **6**, respectively, with aqueous NaOH. In the present case, the reduction product of **11a** was evidently enamino diketone **12a**; its ^1H NMR spectrum lacked the enolic OH, and it was stable to aqueous base but was readily converted to **13a** with oxalic acid in aqueous ethanol.

Scheme I[a]



[a] Key: (a) NH_2OH; (b) H_2, Pt or Pd; (c) $NaBH_4$ + $NiCl_2$/DMF; (d) NaOH; (e) LDA; (f) TMS-Cl; (g) m-$ClC_6H_4CO_3H$; (h) F^-. R = n-$C_{11}H_{23}$ in current work.

Scheme II[a]



[a] Key: (i) $LiAlH_4$; (j) TsOH; (k) B_2H_6, H_2O_2; (l) PCC; (n) $Mo(CO)_4$; (n) $NaBH_4/NiCl_2$, MeOH; (o) H^+; (b) H_2, Pd. R = n-$C_{11}H_{23}$.

The physical data [UV (EtOH) indicate that **13a** exists in the enol form [UV (EtOH) λ_{max} 285 nm (ϵ 7400)] compared to that for **1** λ_{max} 232 nm (ϵ 8500), 272 (10 800)]. ^1H NMR ($CDCl_3$): δ 15.98 (enolic OH). Our value of δ 18.69 for the enolic OH of **1** (Oliver and Lusby, 1988) was recorded in benzene, but Mudd (1981) has reported that δ 18.3 is typical of 1-type compounds in $CDCl_3$.

To try to avoid some of the problems with the reduction of **11a**, we briefly investigated protection of the carbonyl of **11a** as the ethylene ketal **11b**. Catalytic hydrogenation of **11b** cleanly provided enamine **12b**. We had intended to hydrolyze both the enamine and ketal in a single operation; the ketal, however, proved extremely resistant to acid hydrolysis, and treatment of **12b** with oxalic acid in aqueous alcohol was completely selective, giving **13b** with no detectable **13a**. Removal of the ketal from **13b** proved to be exceedingly bothersome. Aqueous acetic acid (Greene, 1981) was ineffective, as was pyridinium p-toluenesulfonate (PPTS) in wet ethanol. Aqueous perchloric acid in THF seemed to destroy **13a** faster than it was formed. The method of Huet et al. (1978)

(sulfuric acid impregnated silica gel in CH_2Cl_2) showed promise, but the hydrolysis was difficult to force to completion, even with the recommended two cycles. The group was finally removed by exchange with acetone, catalyzed by PPTS or H_2SO_4, but with concomitant formation of an unwanted byproduct.

The latter, on the basis of its ^1H NMR and mass spectra, has been identified as the 2,5-dihydroxyalkanophenone **14**. Curiously, **14** seems to cocrystallize with **13a**: A sample of 2:1 **13a**/**14** was recrystallized from hexane (in which pure **13a** is reasonably soluble) to give a first crop consisting (by GLC integration) of **13a**/**14** in a ca. 45:55 ratio; this ratio was unchanged by further recrystallization, first from hexane then from glacial acetic acid. In the absence of systematically determined detector response factors, the ratio is suspiciously close to 1:1.

Finally, we repeated the sequence with the more easily removed (Greene, 1981) ketal derived from propane-1,3-diol. In contrast to **12b**, enamine **12c**, after being allowed to stand overnight in ethanol/water containing oxalic acid, was cleanly converted to **13a** without isolation of **13c**; thus, the 1,3-dioxane appears to the protecting group of choice for this sequence.

EXPERIMENTAL SECTION

Melting points are uncorrected. Mass spectra were obtained from a Finnigan Model 4510 gas chromatograph–mass spectrometer equipped with a 30 m × 0.32 mm (i.d.) DB-1 fused silica column. Electron ionization spectra were collected at 70 eV and a source block temperature of 150 °C. Ammonia chemical ionization spectra were obtained at a source temperature of 60 °C and a reagent gas pressure of 0.5 Torr. The ^1H NMR spectra were obtained on a General Electric QE-300 NMR spectrometer. ^1H chemical shift assignments were made by decoupling experiments. UV spectra were recorded on ca. 1.3×10^{-3} M solutions in 95% ethanol. Gas–liquid chromatography (GLC) was performed with a 15-m DB-1 fused silica capillary column, usually temperature-programmed from 200 to 260 °C. Thin-layer chromatography (TLC) was performed on Whatman 1 in. × 3 in. silica gel plates.

3-Undecyl-4,5,6,7-tetrahydro-4-hydroxy-1,2-benzisoxazole (7) and 3-Undecyl-6,7-dihydro-1,2-benzisoxazole (8). A solu- tion of **2** (Oliver and Lusby, 1988) (10.64 g, 37 mmol) in dry ether (75 mL) was added dropwise to a cold, stirred suspension of $LiAlH_4$ (0.96 g, 25 mmol) in ether (35 mL); after 1.5 h, additional $LiAlH_4$ (0.70 g, 18 mmol) was added in one portion, and after being stirred an additional 1 h, the mixture was allowed to stand overnight at room temperature. Workup and flash chromatography (15–30% EtOAc in hexane) gave 8.67 g (81%) of **7** as a clear oil. Considerable elimination of water from **7** to produce **8** occurred during GLC analysis; however, TLC (8:2 hexane/EtOAc) indicated that alcohol **7** (R_f 0.36) was the main component, with unreacted ketone **2** (R_f 0.56) barely detectable and olefin **8** (R_f 0.77) absent. Mass spectrum, m/z (%): 293 (5, M^+), 276 (15, M – OH), 166 (42), 154 (9), 153 (100), 57 (13), 55 (29).

Because of the ease with which elimination occurred, **7** was not further characterized; rather, the entire sample (8.67 g) in benzene (150 mL) containing *p*-toluenesulfonic acid (200 mg) was refluxed with azeotropic removal of water for 4 h. Although GLC indicated the reaction was complete before this time, premature workup provided a byproduct unstable to GLC whose mass spectrum (solids probe introduction) indicated it to be an ether formed from two molecules of **7** with the loss of H_2O [m/z (%)]: 568 (M^+, 100), 455 (9), 441 (7), 429 (6), 428 (19), 414 (5), 413 (19), 294 (7), 293 (9), 292 (18), 278 (21), 277 (66), 276 (35), 166 (13), 153 (30). When the reaction was complete (monitored by TLC), the cooled solution was washed with 1 M Na_2CO_3, dried over $MgSO_4$, passed through a ca. 2-cm layer of silica gel, and concentrated to dryness to give 7.93 g (97.5%) of **8** as a clear oil that crystallized when chilled. Recrystallization of a sample from 95% EtOH gave pure **8**: mp 33.5–34.5 °C; ^1H NMR ($CDCl_3$) δ 0.88 (3 H, t, CH_3), 1.25 (methylene envelope), 1.65 (2 H, m, H-2′), 2.55 (complex triplet of quartets, H-6), 2.64 (2 H, t, J = 8.7 Hz, H-1′), 2.89 (2 H, t, J = 10 Hz, H-7), 5.69 (1 H, m, H-5), 6.18 (1 H, m, H-4); mass spectrum [m/z (%)] 275 (27 M^+), 176 (20), 163 (14), 162 (90), 148 (31), 135 (51), 134 (19), 122 (13), 121 (100), 94 (11), 93 (28), 71 (19), 69 (11), 67 (16), 66 (24), 65 (18), 57 (75), 55 (46); UV (95% EtOH) [λ_{max} (ϵ)] 202 nm (7100), 234 (6100), 241 (6100), 250 (sh), ca. 260 (sh).

Epoxide 9 and 3-Undecyl-4,5,6,7-tetrahydro-5-hydroxy-1,2-benzisoxazole (10). A solution of 6.86 g (34 mmol) of *m*-chloroperoxybenzoic acid (85%) in CH_2Cl_2 (75 mL) was cooled to 0 °C, 100 mL of saturated aqueous sodium bicarbonate was added, and the two-phase mixture was cooled and stirred while a solution of **8** (7.53 g, 27 mmol) in CH_2Cl_2 (50 mL) was added dropwise. The mixture was allowed to reach room temperature, and after 2 h GLC analysis of an aliquot showed the presence of ca. 10% unreacted **8**. Additional peracid (1.5 g) was added, stirring was resumed for an additional 0.5 h, then the layers were separated, and the organic phase was washed with 1 M Na_2CO_3 and concentrated in vacuo. The residue was taken up in pentane, washed sequentially with cold $NaHSO_3$ and 1 M Na_2CO_3, dried over $MgSO_4$, and concentrated to give 7.54 g of an oil that consisted (by GLC) of 87% **9** and 13% of an earlier eluting impurity, probably 3-undecyl-1,2-benzisoxazole. Epoxide **9** was somewhat unstable and tended to decompose upon attempted column chromatography; accordingly it was used without purification or characterization beyond its mass spectrum [m/z (%)]: 291 (6, M^+), 262 (6), 206 (6), 192 (6), 178 (9), 165 (8), 164 (60), 152 (8), 151 (100), 150 (12), 136 (11), 123 (23), 94 (13), 57 (22), 55 (44).

The entire 7.54 g (ca. 26 mmol) of **9** in 60 mL of Et_2O was added dropwise to a cold, stirred suspension of $LiAlH_4$ (0.99 g, 26 mmol) in Et_2O (50 mL) under N_2. After 1 h, excess $LiAlH_4$ was decomposed by sequential addition of H_2O (1 mL), 15% NaOH (1 mL), and H_2O (3 mL). After workup, 6.25 g of a clear oil was obtained that was subjected to flash chromatography (increasing amounts of EtOAc in hexane); alcohol **10** (4.0 g) was eluted as a clear oil with 40–50% EtOAc and was 97.5% pure by GLC: mass spectrum [m/z (%)] 293 (7, M^+), 222 (5), 208 (9), 194 (17), 180 (7), 167 (6), 166 (47), 154 (10), 153 (100), 124 (5), 109 (8), 57 (16), 55 (26); ^1H NMR ($CDCl_3$) δ 0.88 (3 H, t, CH_3), 1.26 (methylene envelope), 1.64 (2 H, m, H-2′), 1.70 (1 H, s, OH), 2.03 and 1.97 (2 H, m, H-6), 2.36–2.43 (1 H, m, H-4), 2.57 (3H, t, H-1′) 2.68–2.73 (1H, m, H-4), 2.81 (2H, m, H-7), 4.22 (1H, m, H-5).

3-Undecyl-6,7-dihydro-5(4*H*)-keto-1,2-benzisoxazole (11a). A solution of **10** (3.81 g, 13 mmol) in CH_2Cl_2 (25 mL) was added to a stirred suspension of pyridinium chlorochromate (PCC; 5.62 g, 26 mmol) in CH_2Cl_2 (40 mL) at room temperature. After 1 h, an additional 3.0 g of the oxidant was added; 1.5 h later the mixture was filtered through Celite and the filtrate was washed with aqueous $NaHSO_3$, dilute HCl, H_2O, and aqueous Na_2CO_3. After drying and concentration, 3.69 g of a gray oil was obtained that quickly began to crystallize. This material, in 3:1 hexane/EtOAc, was decolorized by passing through a small pad of silica gel and then was recrystallized from hexane: mp 48–48.5 °C; mass spectrum [m/z (%)] 291 (6, M^+), 192 (5), 178 (10), 165 (10), 164 (62), 152 (8), 151 (100), 150 (13), 136 (12), 123 (27), 94 (17), 57 (16), 55 (36); ^1H NMR ($CDCl_3$) δ 0.88 (3 H, t, CH_3), 1.26 (methylene envelope), 1.64 (2 H, m, H-2′), 2.58 (2 H, t, J = 8.6 Hz, H-1′), 2.74 (2 H, t, J = 7.8 Hz, H-7), 3.11 (2 H, t, J = 7.8 Hz, H-6), 3.25 (2 H, s, H-4).

Propylene Ketal (11c). A solution of **11a** (291 mg, 1 mmol), propane-1,3-diol (100 μL, 1.4 mmol), and *p*-toluenesulfonic acid (ca. 10 mg) in toluene (25 mL) was refluxed 130 min with azeotropic removal of water. After concentration, the residue was partitioned between ether/hexane (1:1) and water; the organic phase was washed with aqueous sodium carbonate, dried, and concentrated to give 330 mg (96%) of **11c** as a white solid. A separately prepared sample that was recrystallized from hexane had mp 88.5–89 °C. Data: mass spectrum [m/z (%)] 349 (M^+, 5), 236 (36), 194 (32), 140 (16), 136 (24), 114 (7), 113 (100), 112 (9), 82 (7), 80 (10), 57 (6), 55 (20); ^1H NMR ($CDCl_3$) δ 0.88 (3 H, t, CH_3), 1.26 (methylene), 1.64 (2 H, m, H-3′), 1.79 (2 H, m, H-5″), 2.20 (2 H, t, J = 6.6 Hz, H-7), 2.57 (2 H, t, J = 8.1 Hz, H-2′), 2.72 (2 H, s, H-4), 2.74 (2 H, t, J = 6.6 Hz, H-6), 3.95 (4 H, m, H-4″ and H-5″).

Hydrogenation of 11c. The previous sample of **11c** (330 mg) in 17 mL of 95% EtOH was treated with 50 μL of Et_3N and a few milligrams of 10% Pd on C. Hydrogenation (1 atm) for 1 h gave enamine **12c**. A small sample was removed for ^1H NMR, but the sample was not otherwise characterized: ^1H NMR ($CDCl_3$) δ 0.88 (3 H, t, CH_3), 1.26 (methylene), 1.54 (2 H, m, H-3′), 1.97 (2 H, m, H-5″), 2.18 (3 H, m, H-2′ and H-6), 2.40 (2 H, t, J = 6.9 Hz, H-5), 2.62 (2 H, s, H-3), 3.95 (4 H, m, H-4″ and H-6″).

Conversion of Enamino Ketal 12c to 13a. The alcoholic solution of **12c**, after filtration and removal of ca. 4 mg for ^1H NMR, was treated with 10 mL of 10% aqueous oxalic acid and allowed to stand overnight at room temperature. Dilution with H_2O and extraction with Et_2O/hexane gave, after rinsing with aqueous $NaHCO_3$, drying, and concentration, 278 mg of **13a**. Recrystallization from ca. 70% EtOH gave pure **13a**: mp 56–57.5 °C; mass spectrum [m/z (%)] 294 (M^+, 9), 276 (14), 183 (23), 167 (16), 155 (10), 154 (100), 139 (73), 126 (50), 125 (12), 112 (44), 111 (53), 95 (16), 85 (11), 84 (12), 83 (29), 71 (16), 70 (14), 69 (19), 67 (11), 57 (41), 55 (81); ^1H NMR ($CDCl_3$) δ 0.88 (3 H, t, CH_3), 1.26 (methylene envelope), 1.61 (2 H, m, H-3′), 2.34 (2 H, t, J = 8 Hz, H-2′), 2.60 (2 H, m, H-5), 2.75 (2 H, m, H-6 + H-1), 3.22 (2 H, s, H-3), 15.98 (1 H, s, enolic OH); UV (95% EtOH) λ_{max} 285 nm (ε 7400).

Ethylene Ketal (11b), Enamino Ketal 12b, and Monoketal 13b. The foregoing conditions, but substituting ethylene glycol for propane-1,3-diol, gave ketal **11b**: mp 48–49 °C; mass spectrum [m/z (%)] 335 (M^+, 2.5), 237 (15), 236 (100), 180 (55), 136 (11), 126 (26), 99 (78), 98 (13), 80 (12), 55 (24); ^1H NMR ($CDCl_3$) δ 0.88 (3 H, t, CH_3), 1.25 (methylene envelope), 1.62 (2 H, m, H-2′), 1.99 (2 H, t, J = 7.3 Hz, H-7), 2.55 (2 H, t, J = 8.6 Hz, H-1), 2.59 (2 H, s, H-4), 2.84 (2 H, t, J = 7.1 Hz, H-6), 4.03 (4 H, s, OCH_2CH_2O).

Hydrogenation gave **12b**: mass spectrum [m/z (%)] 337 (M^+, 12), 239 (17), 238 (100), 210 (13), 197 (14), 182 (11), 154 (34), 138 (14), 125 (12), 124 (24), 99 (16), 88 (13), 82 (14), 69 (14), 55 (20); ^1H NMR ($CDCl_3$) δ 0.88 (3 H, t, CH_3), 1.26 (methylene envelope), 1.50–1.55 (2 H, m, H-3′), 1.93 (2 H, t, J = 7.7 Hz, H-6), 2.16 (2 H, m, H-2′), 2.51 (2 H, t, J = 7.7 Hz, H-5), 2.57 (2 H, s, H-3′), 4.01 (4 H, s, -O-CH_2CH_2O-).

Oxalic acid hydrolysis of **12b**, as described for **12c**, cleanly gave **13b**: mp 73–75 °C; mass spectrum [m/z (%)] 338 (M^+, 11), 239 (10), 198 (19), 183 (10), 156 (14), 155 (50), 100 (66), 99 (85), 87 (19), 86 (100), 57 (10), 55 (28); ^1H NMR ($CDCl_3$) δ 0.88 (3 H, t, CH_3), 1.26 (methylene envelope), 1.6 (2 H, m, H-3′), 1.85 (2 H, t, J = 8.0 Hz, H-6), 2.32 (2 H, t, J = 8 Hz, H-2′), 2.56 (overlapping singlet (H-3) and triplet (J = 8 Hz, H-5), 4.02 (4 H, s, OCH_2CH_2O).

Deketalization of 13b. A solution of **13b** (507 mg) in acetone (18 mL) was treated with concentrated H_2SO_4 (ca. 25 μL). After the mixture was allowed to reflux a total of 160 min and stand overnight at room temperature, concentration and partitioning gave 438 mg of a yellow solid that was crystallized from EtOH/H_2O to give 227 mg of a light yellow material after prior softening: mp ca. 93–99 °C; TLC (7:3 hexane/EtOAc) R_f 0.66 and 0.61. GLC indicated a ca. 2:1 ratio of **13a** and **14**. Recrystallization from hexane gave 129 mg that was 56:44 **13a**/**14** by GLC; subsequent recrystallization, first from hexane and then from HOAc, did not alter this ratio. Mass spectrum of **14** [m/z (%)]: 292 (M^+, 12), 274 (20), 189 (29), 165 (25), 152 (38), 147 (10), 138 (7), 137 (100), 109 (13), 81 (14), 55 (28). The ^1H NMR spectrum of **14** was obtained by subtracting the spectrum of pure **13a** from that of a ca. 1:1 mixture of **13a** and **14**. The subtraction routine employed was one supplied by the instrument manufacturer. ^1H NMR of **14** ($CDCl_3$): δ 0.88 (3 H, t, CH_3), 1.27 (methylene), 1.74 (2 H, t, J = 6.9 Hz, H-3′), 2.93 (2 H, t, J = 7.2 Hz, H-2′), 6.89 (1 H, d, J = 8.7 Hz, H-6), 7.02 (1 H, dd, J = 2.1 and 8.7 Hz, H-5), 7.22 (1 H, d, J = 2.1 Hz, H-3).

ACKNOWLEDGMENT

We appreciate the skilled assistance of Dawn J. Harrison and Kristina Strupczewski.

LITERATURE CITED

Arai, K.; Mito, N.; Morita, K.; Hirata, N. Preparation, formulation, and testing of Herbicidal 5-[2-(fluorophenylthio)ethyl]cyclohexane-1,3-diones. Eur. Patent Appl. EP 254, 514, Jan 27, 1988; *Chem. Abstr.* **1988**, *109*, 37607y.

Chevron Research Co. Preparation of Herbicidal 2-(1-oximinobutyl)-5-[2-(ethylthio)propyl]cyclohexane-1,3-diones. Israeli IL 69, 328, Oct 31, 1986; *Chem. Abstr.* **1987**, *107*, 197622m.

Greene, T. W. *Protective Groups in Organic Synthesis*; Wiley: New York, 1981; pp 121–129.

Huet, F.; Lechevallier, A.; Pellet, M.; Conia, J. M. Wet Silica Gel; a Convenient Reagent for Deacetalization. *Synthesis* **1978**, 63–65.

Jurenka, R. A.; Neal, J. W., Jr.; Howard, R. W.; Oliver, J. E.; Blomquist, G. J. In vitro Inhibition of Prostaglandin Synthase by Compounds from the Exocrine Secretion of Lace Bugs. *Comp. Biochem. Physiol. C* **1989**, in press.

Knudsen, C. G.; Michaely, W. J. Herbicidal 3-(substituted oxy)-2-benzoylcyclohex-2-enones, their formulations, and processes for their preparation. Eur. Pat. Appl. EP 253, 124, Jan 20, 1988; *Chem. Abstr.* **1988**, *109*, 37606x.

Lusby, W. R.; Oliver, J. E.; Neal, J. W., Jr.; Heath, R. R. Isolation of the Major Component of Setal Exudate from *Corythucha ciliata*. *J. Nat. Prod.* **1987**, *50*(6), 1126–1130.

Lusby, W. R.; Oliver, J. E.; Neal, J. W., Jr.; Heath, R. R. Acylcyclohexanediones from the Setal Exudate of Hawthorn Lace Bug Nymphs *Corythucha cydoniae* (Hemiptera: Tingidae). *J. Chem. Ecol.* **1989**, *15*, 2369–2378.

Mudd, A. Novel β-Triketones from Lepidoptera. *J. Chem. Soc., Chem. Commun.* **1978**, 1075-1076.

Mudd, A. Novel 2-Acylcyclohexan-1,3-diones in the Mandibular Glands of Lepidopteran Larvae. Kairomones of *Ephestia kuehniella* Zeller. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2357–2362.

Mudd, A. Synthesis of Kairomonal 2-Acylcyclohexane-1,3-dione Components of Larval Mandibular Glands of *Ephestia kuehniella*. *J. Chem. Ecol.* **1985**, *11*, 251–256.

Nemoto, T.; Shibuya, M.; Kuwahara, Y.; Suzuki, T. New 2-Acylcyclohexane-1,3-diones: Kairomone Components against a Parasitic Wasp, *Venturia canescens*, from Feces of Almond Moth, *Cadra cautella*, and the Indian Meal Moth, *Plodia interpunctella*. *Agric. Biol. Chem.* **1987**, *51*(7), 1805–1810.

Nitta, M.; Kobayashi, T. Reductive Ring Opening of Isoxazoles with $Mo(CO)_6$ and Water. *J. Chem. Soc., Chem. Commun.* **1982**, 877–878.

Oliver, J. E.; Lusby, W. R. Synthesis of 2-Acyl-3,6-dihydroxy-2-cyclohexen-1-ones. *Tetrahedron* **1988**, *44*(6), 1591–1596.

Wakefield, B. J.; Wright, D. J. Isoxazole Chemistry Since 1963. *Adv. Heterocycl. Chem.* **1979**, *25*.

Received for review December 15, 1988. Accepted May 23, 1989.