Synthesis of Substituted Truxillic Acids from p-Coumaric and Ferulic Acid: Simulation of Photodimerization in Plant Cell Walls

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4,4'-Dihydroxy-3,3'-dimethoxy-α-truxillic acid (II) and 4,4'-dihydroxy-3-methoxy-α-truxillic acid (III) were prepared and isolated for the first time in good yield from photodimerization of (E)-ferulic acid (F) alone and mixed with (E)-p-coumaric acid (P) (for III and II, respectively) using high-intensity fluorescent light. The rate of photodimerization of ferulic acid alone was much slower than the dimerization of P to 4,4'-dihydroxy-α-truxillic acid (I). When p-coumaric acid was added to ferulic acid, the rate of production of II was increased; the proportions of I-III formed varied with the ratio of P:F irradiated. These results are discussed in relation to photodimerization experiments with carbohydrate esters of ferulic and p-coumaric acids obtained from grass cell walls and in relation to the proportions of cyclodimers obtained from grass cell walls.

INTRODUCTION

Recent work has shown that substituted truxillic and truxinic acids are bound to the cell walls of graminaceous plants e.g., Italian ryegrass, coastal Bermuda grass, and various tropical grasses (Hartley et al., 1988, 1990a; Ford and Hartley, 1990). It has been suggested that these acids are formed in the cell walls by dimerization of p-coumaroyl and feruloyl groups that are ester-linked to the arabinoxylans of the walls (Hartley et al., 1988, 1990b and Hartley and Ford, 1989). This dimerization process is believed to decrease cell wall biodegradability, which leads to low rates of production of ruminant meat, milk, and wool.

Theoretically, dimerization of p-coumaric acid (P) or ferulic acid (F) or a mixture of the two can produce a total of 36 substituted truxillic and truxinic acid stereoisomers depending on whether "head-to-tail" (ht) or "head-to-head" (hh) dimerization occurs (Hartley et al., 1990a). In the cell walls so far examined, 4,4'-dihydroxy-α-truxillic acid (I) (a PPht dimer), 4,4'-dihydroxy-3,3'-dimethoxy-α-truxillic acid (II) (an FFht dimer), and 4,4'-dihydroxy-3-methoxy-α-truxillic acid (III) (a PFht dimer) were the major dimers identified (Eraso and Hartley, 1990; Ford and Hartley, 1990; Hartley et al., 1988, 1990a) (Figure 1).

Cohen et al. (1964) prepared I by photodimerization of crystalline p-coumaric acid. Under similar lighting conditions, no dimerization of crystalline ferulic acid occurred (Hartley et al., 1988; Ford and Hartley, 1989), probably due to the monomers being too far apart in the crystal lattice. A distance of less than about 4 Å between the double bonds in the side chain of the two monomers is required for dimerization to occur (Cohen et al., 1964; Egerton et al., 1981; Kan, 1966; Reiser and Egerton, 1979; Schmidt, 1964). Irradiation of a thin layer of ferulic acid with a combination of fluorescent and incandescent light gave a very low yield (ca. 2%) of an FF dimer (Ford and Hartley, 1989). These workers also showed that a mixture of p-coumaric plus ferulic acid gave a similar yield (ca. 3%) of a suspected PF dimer. The two dimers were not isolated, and their steric configurations were not determined.

In the present work, methods have been devised to obtain II and III preparatively from p-coumaric and ferulic acid and their steric configurations determined. The
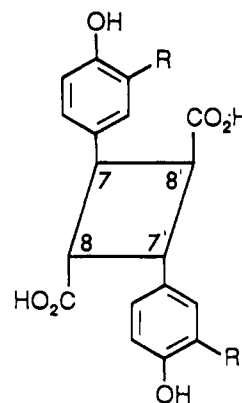

Figure 1. I, R = R' = H (4,4'-dihydroxy-α-truxillic acid); II, R = R' = OMe (4,4'-dihydroxy-3,3'-dimethoxy-α-truxillic acid); III, R = OMe, R' = H (4,4'-dihydroxy-3-methoxy-α-truxillic acid).

effect of varying the ratio of the p-coumaric and ferulic acid reactants on dimer formation has also been investigated.

MATERIALS AND METHODS

(E)-p-Coumaric and (E)-ferulic acids were obtained commercially. p-Coumaric acid was used as received, and ferulic acid was recrystallized from water. Photodimerizations were carried out using fluorescent light (Sylvania fluorescent "cool white", 394 μEinsteins m^{-2} s^{-1}) (Hartley et al., 1990b) under nitrogen to prevent oxidation.

Samples (1-2 μg) were prepared for gas chromatographic (GLC) analysis by adding 10 μL of dry pyridine and 10 μL of bis(trimethylsilyl)trifluoroacetamide (BSTFA), shaking, and allowing to stand for 5 min. GLC analysis of the silyl derivatives was conducted on a Perkin-Elmer 2100 equipped with an Analabs GB-1 fused silica column (50 m × 0.25 mm i.d.) and a FID (350 °C) with He as the carrier gas (0.5 mL/min). The injector temperature was 300 °C and the column oven held at 170 °C for 5 min and then programmed from 170 to 325 °C at 4 °C/min. Retention times of the truxillic acids were identical to those previously reported (Hartley et al., 1990a). Peaks were measured with a Perkin-Elmer LCI 100 computing integrator. Silylated derivatives were characterized by GC-EIMS using a Perkin-Elmer Sigma 300 GC with a cold on-column injector interfaced to an Extrel 50/400 quadrapole mass spectrometer. The derivatives were separated on a DB-1 fused silica column (30 m × 0.25 mm i.d.) with He as the carrier gas at 7.0 psi. The column was programmed from 50 to 260 °C at a rate of 10 °C/min. MS

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Table I. Yield of Photodimers Derived from (E)-p-Coumaric and (E)-Ferulic Acids (Percent of Original Monomer Converted)[a]

acid	irradiation, h			
	32	96	336	480
(E)-p-coumaric	96			
(E)-ferulic	tr[b]	2	33	50

[a] Determined by GLC. [b] Trace.

conditions were ion source, 150 °C, and ionizing voltage, 70 eV. Underivatized samples were analyzed using a direct insertion probe. Data were collected using a Technivent interface and software package and processed with an IBM PC. [1]H nuclear magnetic resonance (NMR) spectra were obtained using a Bruker MSL-300 NMR spectrometer for compounds I and II and an AM-500 spectrometer for compound III. The samples (1–4 mg) were dissolved in pyridine-d_5 (99.96%) (0.4 mL) in a 5 mm o.d. NMR tube. Chemical shifts were referenced to Me$_4$Si at 0 ppm. Data reported were obtained by iteration utilizing Bruker's PANIC program on observed values from spectra Lorentz–Gaussian function (LB = –0.2, GB = 0.3) prior to Fourier transformation.

4,4′-Dihydroxy-α-truxillic Acid (I) and 4,4′-Dihydroxy-3,3′-dimethoxy-α-truxillic Acid (II). (E)-p-Coumaric or (E)-ferulic acid (300 mg) was dissolved in methanol (100 mL) and transferred to a 5-L round-bottom flask, and the solvent was evaporated in vacuo. The sample was irradiated for the time indicated (Table I). p-Coumaric acid was 96% dimerized after 32 h of irradiation as estimated by GLC of the silyl derivatives. Every 80 h (for ferulic acid), the sample was redissolved in methanol and the solvent evaporated on a rotary evaporator. The irradiation was then continued. After the first 80–160 h, the reside was no longer crystalline but was deposited as a thin, oily film on the surface of the flask. Samples were checked periodically by GLC of the silyl derivatives for the formation of dimer and disappearance of monomer. Upon termination of the reaction, the residue was dissolved in methanol and transferred to a 50-mL round-bottom flask, and the solvent was evaporated, leaving an oily residue. The residue was dissolved in diethyl ether and the solvent evaporated, leaving a white solid. The solid was washed with ether (25 mL) to remove any remaining monomer, leaving the cyclodimers in excess of 98% purity. Dimer I: yield 294 mg (98%); mp 300 °C with decomposition (lit. 340 °C with a rapid temperature rise); ^{1}H NMR δ (number of protons) 4.51 (2), 4.99 (2), 7.19 (4), 7.70 (4); mass spectrum [major ions, m/e (relative percent)] (TMS derivative) 73 (100), 308 (86.7), 293 (53.0), 219 (37.6), 75 (26.0), 309 (22.3), 294 (15.6), 249 (11.3), 179 (11.3), 77 (10); (direct insertion probe) 44 (100), 164 (86.8), 91 (64.5), 120 (34.2), 107 (30.6), 119 (29.1), 147 (28.0), 163 (25.0), 104 (22.5), 118 (22.3). Dimer II: yield 40 mg (13%); mp 277–279 °C with decomposition; ^{1}H NMR δ (number of protons) 3.75 (6), 4.55 (2), 5.03 (2), 7.24 (2), 7.36 (2), 7.45 (2); mass spectrum [major ions, m/e (relative percent)] (TMS derivative) 338 (100), 73 (28.2), 323 (24.5), 339 (23.0), 249 (16.6), 308 (12.8), 340 (11.2), 293 (8.8), 219 (7.4), 324 (7.0); (direct insertion probe) 194 (100), 77 (50.6), 44 (48.5), 89 (28.7), 78 (21.7), 40 (21.5), 133 (21.5) 91 (19.5), 107 (19.3), 179 (17.6), 105 (17.4), 63 (17.3).

4,4′-Dihydroxy-3-methoxy-α-truxillic Acid. (III). (E)-p-Coumaric acid (200 mg) and (E)-ferulic acid (50 mg) were placed in a 5-L round-bottom flask and dissolved in methanol, and the solvent was evaporated in vacuo using a rotary evaporator. The acids were deposited as a thin, crystalline film on the flask. The sample was irradiated for a total of 96 h. The residue was dissolved and the solvent evaporated after 32 and 64 h. As the reaction progressed, the mixture did not crystallize and was deposited as an oil. Upon completion of the reaction, the residue was dissolved in methanol and transferred to a 50-mL round-bottom flask, and the solvent was evaporated. GLC analysis showed 88% conversion to the three dimers I (65%), III (22%), and II (1%). The solid was stored under ether overnight. The ether layer contained 30% I, 40% III, and 8% II. Separation of the three cyclodimers in the ether layer was achieved using An-altech 20 cm × 20 cm precoated (0.25 mm) silica gel (10 μm) plates with calcium sulfate as a binder. The plates were activated at 110 °C for 30 min and stored in a desiccator. Samples (3 mg)

Table II. Yield of Photodimers Derived from Irradiation of Mixtures of (E)-p-Coumaric and (E)-Ferulic Acids[a]

monomer acids, mol %		irradiation, h	monomer, %, converted to dimers	yield of dimers, % of reaction mixture		
p-coumaric	ferulic			I	II	III
11.5	88.5	48	11.0	tr[b]	7.3	1.5
		112	34.0	1.5	25.2	6.8
		128	41.5	2.5	30.0	8.6
50.0	50.0	160	68.0	17.9	13.3	27.8
78.2	21.8	96	78.0	52.5	1.9	21.4
83.0	17.0	96	88.0	65.0	1.0	22.1

[a] Determined by GLC (average of duplicate samples). [b] Trace.

were dissolved in methanol (5 mL) and applied to each plate using a Desaga automated applicator. The plates were developed using chloroform/glacial acetic acid/water (50/45/4 v/v) and dried for 24 h. A portion of each plate was visualized by spraying a strip 2.0 cm wide with diazotized p-nitroaniline followed by 10% (w/v) potassium carbonate (Stahl, 1969). The three truxillic acids gave blue-purple colorations under these conditions. Compound III was recovered from the plate by extraction of the desired band with methanol. R_f values were 0.67, 0.72, and 0.80 for I, III, and II, respectively. About 5 mg of III was isolated: mp 270 °C with decomposition; ^{1}H NMR δ (number of protons) 3.74 (3), 4.50 (1), 4.55 (1), 5.00 (1), 5.01 (1), 7.19 (2), 7.23 (1), 7.36 (1), 7.44 (1), 7.70 (2); mass spectrum [major ions, m/e (relative percent)] (TMS derivative) 338 (100), 73 (37.7), 323 (21.5), 339 (20.1), 293 (19.6), 308 (16.8), 340 (9.4), 219 (8.8), 249 (7.0), 324 (6.5); (direct insertion probe) 44 (100), 91 (90.0), 77 (83.0), 65 (61.0), 107 (52.5), 89 (51.0), 120 (50.0), 164 (47.0), 147 (30.0), 150 (27.5).

Dimerization of Mixtures of (E)-p-Coumaric and (E)-Ferulic Acids. Varying amounts of p-coumaric and ferulic acids were placed in a 5-L round-bottom flask and dissolved in methanol, and the solvent was removed using a rotary evaporator, depositing the mixture of acids as a thin, crystalline film. The samples were irradiated for the times indicated (Table II). Samples were redissolved and evaporated as above after every 32 h of irradiation. As the reaction progressed, the samples did not crystallize and were deposited as an oil. The progress of the reaction was followed by GLC of the silylated residues of aliquots taken at the times indicated in Table II.

RESULTS AND DISCUSSION

The conversion of (E)-ferulic acid to its cyclodimer II is considerably slower than the conversion of (E)-p-coumaric acid to I, as can be seen in Table I. Ferulic acid required 480 h for 50% conversion compared to only 32 h for p-coumaric acid to be almost completely converted to I. The conversion of ferulic acid was achieved by preparing a fresh surface for irradiation every 32 h by dissolving the residue in methanol and then removing the solvent. After two to three cycles, the residue failed to crystallize and was deposited as an oil. The yield was higher than previously reported (Ford and Hartley, 1989), probably because in the present work the material did not crystallize and thus allowed more of the side-chain double bonds to be sufficiently close to undergo dimerization. In a control study in which the need for dissolution and evaporation steps was established, a thin film of ferulic acid was irradiated for 228 h and the conversion to dimer compared with results from a sample which had been dissolved and evaporated four times. After 228 h, the original thin film showed only 2% conversion to dimer as compared to 41% for the sample which had undergone the dissolution and evaporation steps. Formation of fresh surfaces by dissolving the sample probably led to redistribution of the monomer molecules, thus allowing further reaction to take place.

Purification of the dimer fraction after irradiation was accomplished by dissolving the oil in ether followed by

Table III. NMR Data for Cyclobutane Ring Protons[a]

R	R'	compd	chemical shifts,[b] ppm				coupling constants, Hz					
			H_7	$H_{7'}$	H_8	$H_{8'}$	$^3J_{7,8}$	$^3J_{7'8'}$	$^3J_{7,8'}$	$^3J_{7',8}$	$^4J_{7,7'}$	$^4J_{8,8'}$
H	H	I	4.99	4.99	4.51	4.51	10.40	10.86	7.09	7.15	−0.40	−1.25
OCH₃	OCH₃	II	5.03	5.03	4.55	4.55	10.34	10.33	7.74	7.04	−0.48	−0.32
OCH₃	H	III	5.01	5.00	4.55	4.50	10.58	10.00	7.12	7.13	−0.70	−1.11

[a] Calculated using Bruker's PANIC program. [b] In pyridine-d_5 referenced to Me₄Si.

Table IV. Distribution of Substituted Cyclobutane Dimers Derived from Plant Cell Walls, from Irradiated Mixtures of (E)-p-Coumaroyl and (E)-Feruloyl Trisaccharide Esters (PAXX and FAXX), and from Irradiated Mixtures of Pure (E)-p-Coumaric (P) and (E)-Ferulic (F) Acids

	cell walls[a]		irradiated mixtures		
	coastal Bermuda grass	tall fescue	PAXX + FAXX[b]	P	+	F
monomers,[c] mol % of P + F						
(E)-p-coumaric	60.3	44.6	45.5	78.0		50.0
(E)-ferulic	39.7	55.4	54.5	22.0		50.0
dimers,[d] % of total dimers						
I + II + III	62.5	61.5	87.7	94.0		95.3
all other cyclobutane dimers	37.5	38.5	12.3	6.0		6.5
dimers,[d] mol % of I + II + III						
I	55.0	35.5	41.8	71.3		32.7
II	25.5	42.3	12.5	2.0		20.6
III	19.5	22.2	45.6	26.7		46.9
monomers converted to dimers, %	~10	~10	~50	~96		~68

[a] Monomers and dimers obtained by NaOH treatment of cell walls (Hartley and Morrison, 1991). [b] Dimers obtained by NaOH treatment of irradiated PAXX + FAXX (Hartley et al., 1990b). [c] P and F (in cell walls), in PAXX + FAXX and in P + F (before dimerization). [d] After irradiation of PAXX + FAXX and P + F.

removal of solvent. The crystalline material was stored under ether for 16 h. Unreacted monomer dissolved, leaving II in excess of 95% pure. Although the yield of II after irradiation was determined by GLC to be ca. 50%, the isolated yield was ca. 23%.

Dimer I was prepared according to the same procedure as II, but only 32 h of irradiation was required to achieve 96% conversion of monomer to dimer. Dimers I–III were shown to be the α head-to-tail truxillic acids shown in Figure 1 on the basis of a combination of MS and NMR data. A head-to-head orientation would show symmetrical as well as asymmetrical splitting in their mass spectra. Asymmetrical splitting of the silylated cyclodimers would produce mass peaks at m/z 356, 416, and 386 for dimers I, II, and III, respectively (Ford and Hartley, 1989). These peaks are absent in the mass spectra of these compounds. Two types of trans–trans head-to-tail orientations are possible: one in which the aromatic and carboxyl groups of the parent acids are on opposite sides of the cyclobutane ring (α-truxillic acids as in Figure 1) and one with the aromatics on one side of the ring and the carboxyls on the other (ϵ-truxillic acids). The NMR data (Table III) then establish that the 7,8 and 7',8' protons are trans and that the 7,8' and 7',8 protons are cis relative to each other. This is indicated directly by three-bond scalar coupling (^3J) data that gives values of ca. 10–11 Hz and ca. 7–8 Hz, respectively. Further confirmation is provided by the negative values calculated for the four-bond scalar coupling constants (^4J), which indicate a trans diagonal relationship for protons 7,7' and 8,8'. This is consistent with the results obtained by Montaudo and Caccamese (1973) for chalcone photodimers which give the α-truxillic structure from trans-cinnamic acids. Although this is the first report of the isolation of II and III, Cohen et al. (1964) isolated I earlier and determined its stereochemical structure by X-ray diffraction analysis.

Products from irradiation of mixtures of p-coumaric and ferulic acids were monitored by GLC with the aim of finding the simplest method for the preparation of III. Since the formation of I from p-coumaric acid was considerably faster than the formation of II from ferulic

acid, it seemed likely that a mixture of predominantly ferulic acid (90% by wt) with 10% p-coumaric acid might produce mainly III. In fact, this mixture gave mainly II (Table II). The conversion rate of ferulic acid in this system to II was 30% after 128 h of irradiation. This was a higher conversion of ferulic acid to II than when the acid alone was irradiated. Pure ferulic acid required 336 h to achieve 33% conversion to II.

When p-coumaric acid was the predominant monomer in mixtures with ferulic acid, the main dimer produced was I together with some III and a small amount of II (Table II). The highest yield of III was obtained from an equimolar mixture of the two parent acids (Table II). Since III is more soluble in ether than I or II, the concentration of III in the reaction mixture used for this isolation was increased with respect to that of I and II from 22 to 40% by allowing the crystalline product (mixtures of I–III) to stand overnight in ether. The ether layer enriched with III was then evaporated, the residue was dissolved in methanol, and the dimers were separated by preparative TLC.

Table IV compares the distribution of substituted cyclobutane dimers derived from plant cell walls from (E)-p-coumaroyl and (E)-feruloyl trisaccharide esters and from mixtures of pure p-coumaric and ferulic acids. The dimerization products from equimolar concentrations of p-coumaric and ferulic acids are similar to those derived from the dimerization of O-[5-O-((E)-p-coumaroyl)-α-L-arabinofuranosyl]-(1→3)-O-β-D-xylopyranosyl-(1→4)-D-xylopyranose (PAXX) and O-[5-O-((E)-feruloyl)-α-L-arabinofuranosyl]-(1→3)-O-β-D-xylopyranosyl-(1→4)-D-xylopyranose (FAXX) (Hartley et al., 1990b). The two esters were obtained by treatment of coastal Bermuda grass cell walls with a mixture of cell wall degrading enzymes (Borneman et al. 1990). Thus, a mixture of ferulic acid plus p-coumaric acid (ca. 1:1) or of FAXX plus PAXX (ca. 1:1) gave a similar product distribution of I–III (Table IV). In both cases comparatively small amounts of the dimer fraction (6.5 and 12.5% for dimerized p-coumaric acid plus ferulic acid and for PAXX plus FAXX,

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respectively) were represented by substituted cyclobutane stereoisomers of the two parent acids other than I–III.

These findings may be compared with the products from the treatment of cell walls of coastal Bermuda grass and Kentucky 31 tall fescue with sodium hydroxide (Hartley and Morrison, 1991) (Table IV). The ratio F:P was 0.6 (coastal Bermuda grass) or 1.2 (tall fescue), but the proportions of I plus II plus III were similar, as were the yields of other cyclobutane dimers of the PP, PF, and FF types (representing ~38% of the total dimers) (Table IV). The total percentage of cyclodimers of the PP, PF, and FF types accounted for only about 10% of the p-coumaric and ferulic acids found in these cell walls. Dimerization of the low molecular weight acids or esters (i.e., PAXX and FAXX) gave higher yields of dimers than those found in the cell walls. Within the cell walls, it appears that the proportion of dimers formed from monomers is limited by the number of monomers which are sufficiently close to react. This limitation is less important with the low molecular weight compounds when the mixture to be irradiated is redistributed by the dissolution and evaporation cycles. As the complexity of the matrix within which the monomers are held was increased from the pure acids to PAXX and FAXX to plant cell walls, the percentage of cyclobutane dimers other than I–III increased. This is probably due to an increase in the restriction of movement of the monomer units, forcing the production of the minor dimers. The proportions of these cyclodimers provide a possible key to the original location of the monomers in the plant as they depend on the spatial distribution of ester-linked p-coumaric and ferulic acids. The present work has shown that substituted cyclobutane dimers that cannot be formed by irradiation in the crystalline state can be obtained preparatively from the noncrystalline phase.

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