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SYNTHESES AND SPECTRAL STUDIES OF SOME DIENIC AND ENYNIC ESTERS

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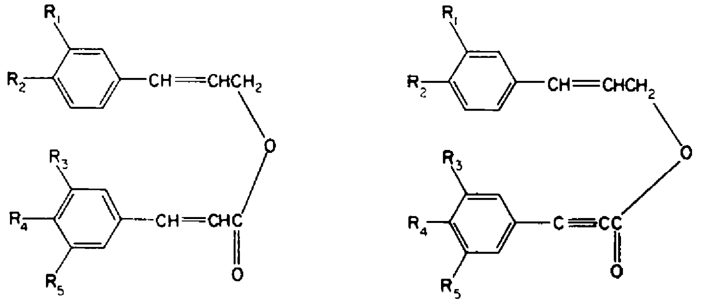
Abstract—Syntheses of dienic esters of the *trans*-cinnamyl *trans*-cinnamate and *trans*-cinnamyl *cis*-cinnamate types and enynic esters of the *trans*-cinnamyl phenylpropiolate and phenylpropargyl *trans*-cinnamate types are described. Characteristic UV, IR and NMR absorption bands are noted.

Bloomfield and Fuchs[1] reported the syntheses and UV absorption spectra (as well as some other properties) of a series of substituted ethyl *cis*- and *trans*-cinnamates and ethyl phenylpropiolates. However, the only analogous ester of the cinnamyl type I, II, or III which seems to have been reported is the parent *trans*-cinnamyl *trans*-cinnamate itself (Ia), a natural product obtained from *Storax*,[2] Perubalsam,[2] the buds of *Populus balsamifera*,[3] and the berries of *Lavungo scandens*.[4]



I: *trans,trans*
II: *trans,cis*
III: *trans*

a: $R_1 = R_2 = R_3 = R_4 = R_5 = H$
b: $R_1R_2 = —OCH_2O—$, $R_3 = R_4 = R_5 = CH_3O$
c: $R_1R_2 = R_3R_4 = —OCH_2O—$, $R_5 = H$
d: $R_1R_2 = —OCH_2O—$, $R_3 = R_4 = CH_3O$, $R_5 = H$
e: $R_1 = R_2 = R_3 = R_4 = CH_3O$, $R_5 = H$

These dienic and enynic esters as well as phenylpropargyl *trans*-cinnamate (IV), and its derivatives are of interest as open-chain isomers and possible precursors of lignan lactones.[5] We report here the syntheses and spectral investigations (UV, IR, and NMR) of a number of these esters.

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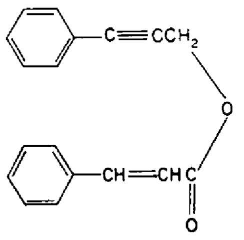
[1] J. J. Bloomfield and R. Fuchs, *J. Org. Chem.* **26**, 2991 (1961).

[2] *Beilsteins Handbuch der Organischen Chemie* Vol IX; p. 585. Julius Springer, Berlin (1926).

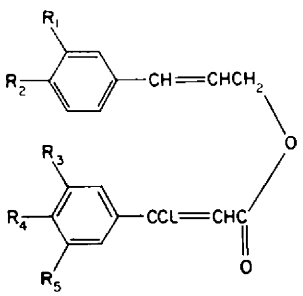
[3] A. Goris and H. Canal, *Bull. Soc. Chim. Fr.* **3**, 1982 (1936).

[4] K. K. Baslas and S. S. Deshapande, *J. Indian Chem. Soc.* **27**, 379 (1950); K. K. Baslas, *Perfumery Essent. Oil Record* **50**, 124 (1959) [*Chem. Abstr.* **53**, 16476 (1959).]

[5] L. H. Klemm and K. W. Gopinath, *Tetrahedron Letters* 1243 (1963).



IV *trans*



V

3,4-Methylenedioxy- and 3,4,5-trimethoxyphenylpropiolic acids were derived from the corresponding cinnamic acids by the successive steps of Fischer esterification with methanol or ethanol, addition of bromine to the double bond, and subsequent dehydrobromination with alcoholic potassium hydroxide. Overall yields for the propiolic acids were 51% and 33%, respectively. When the dibromo ester from 3,4-methylenedioxycinnamate was treated with hot (but not refluxing) alcoholic potassium hydroxide, it was found that monodehydrobromination occurred to give a precipitate of potassium 2-bromo-3-(3,4-methylenedioxyphenyl)acrylic acid in quantitative yield. The overall yield for formation of the propiolic acid, however, was the same whether the dehydrobromination was accomplished in one or two stages.

For preparation of the cinnamyl esters of cinnamic and phenylpropiolic acids, one cannot employ the Fischer method since the cinnamyl alcohol may give replacement of the allylic alcoholic function as well as dimerization through the carbon-carbon double bond.[6] For the *trans*-cinnamic acids, esterification was successfully accomplished in yields of 61–86% by first forming the acid chloride (by means of excess thionyl chloride) and then treatment thereof with the cinnamyl alcohol in a large excess of pyridine. This same procedure could not be used, however, for synthesis of cinnamyl phenylpropiolates III, since hydrogen chloride, a by-product of acid chloride formation, added to the triple bond of the acid in the first step, and excess pyridine caused the formation of resinous materials (to the virtual exclusion of desired ester) in the second. Formation of such resinous products was avoided by use of only a small volume (but still an excess) of pyridine. Then in the first step, by allowing the solid acid to stand with excess thionyl chloride at room temperature until a clear solution resulted, it was possible to prevent addition to the triple bond provided that (a) the thionyl chloride used was fresh, reagent grade and that (b) the dissolution process was complete in a relatively short time. In cases where both conditions (a) and (b) were not met, the esterification product isolated was either the chlorodienic ester V or a mixture of V and III. Yields of the enynic esters obtained were 44% for IIIb and 36% for IIId, while accompanying the formation of IIIc (25% yield) was also Vc (21% yield). Structure V was assigned to the chlorodienic compounds on the bases of IR (no absorption for the triple bond) and NMR spectra (no absorption—at ca. 7·7 ppm—for the presence of a proton on the β-carbon of the acid moiety).

trans-Cinnamyl *cis*-cinnamates were obtained in 43–84% yields by selective hydrogenation of the enynic esters in ethyl acetate, at atmospheric pressure and in the presence of Lindlar catalyst.

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[6] K. Freudenberg and O. Ahlhaus, *Monatsh.* **87**, 1 (1956).

Phenylpropargyl *trans*-cinnamate (IV) was prepared (in 65% yield) by the method used for the *trans,trans* dienic esters. Structural assignment was based on IR and NMR spectra. In contrast to the strong IR absorption band for the triple bond in III, there was very weak absorption[7] for this bond in IV. Since the NMR spectrum was completely consistent with structure IV (Experimental), the possibility that the weak absorption for the triple bond was due to the presence of a non-acetylenic compound as the major component of the sample was eliminated.

EXPERIMENTAL

UV spectra were determined in 95% ethanol by means of a Cary Model 11 spectrophotometer. IR spectra were obtained by means of a Beckman IR-7 spectrophotometer. NMR spectra were obtained by means of a Varian A-60 spectrometer using tetramethylsilane as an internal standard. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Illinois.

3,4-Methylenedioxy-[8] and 3,4-dimethoxycinnamic[9] acids were prepared from piperonal and 3,4-dimethoxybenzaldehyde, respectively, by means of the Knoevenagel reaction. 3,4,5-Trimethoxycinnamic acid was purchased from Aldrich Chemical Co., Milwaukee, Wisconsin. Methyl and ethyl esters of these acids were prepared by refluxing solutions of the acids in freshly prepared 3% (w/w) hydrogen chloride in anhydrous methanol and ethanol,[10] respectively, and recrystallization of the products to narrow melting ranges.

Substituted trans-*cinnamyl alcohols.* To a cold (below −5°) mixture of 5·6 g $LiAlH_4$ in 500 ml anhydrous ether was added dropwise, with stirring, over a period of 45 min a solution of 18–20 g ethyl 3,4-dimethoxy- or 3,4-methylenedioxycinnamate in 200 ml ether. After 5 hr of additional stirring, enough water was added (cautiously) to form a slurry. From the washed and dried supernatant ethereal layer and extracts of the slurry was obtained a residue which was recrystallized from benzene–petrol (30–60°), yield ca. 12 g alcohol (76–81%), m.p. range 1–2°.

trans-*Cinnamyl* trans-*cinnamates*

trans-3,4-*Dimethoxycinnamyl* trans-3,4-*dimethoxycinnamate* (Ie). A mixture of 3,4-dimethoxycinnamic acid (5 g), benzene (50 ml), and thionyl chloride (12 ml, reagent grade) was refluxed for 5 hr, during which time the acid slowly dissolved. Excess thionyl chloride was removed by repeated distillation (*in vacuo*) with benzene. A solution of the residual acid chloride in 20 ml benzene was refluxed for 15 hr with a solution of 5 g 3,4-dimethoxycinnamyl alcohol in 50 ml pyridine. The cooled solution was washed successively with water, dil. HCl aq., water, dil. Na_2CO_3 aq. and water. The residue from evaporation of the dried benzene solution crystallized from ethanol as needles, yield 7·9 g (86%), m.p. 78–80°, raised to 80–81° on recrystallization. (Found: C, 68·87; H, 6·26. $C_{22}H_{24}O_6$ requires: C, 68·73; H, 6·29%).

trans-3,4-*Methylenedioxycinnamyl* trans-3,4,5-*trimethoxycinnamate* (Ib). A mixture of 3,4,5-trimethoxycinnamic acid (6 g), benzene (30 ml), thionyl chloride (2 ml), and pyridine (6 drops) was refluxed for 5 hr, allowed to stand overnight, and evaporated to dryness. The resultant orange solid acid chloride was esterified (using 5 g of the alcohol component) as for Ie, but processing consisted instead of removal of crystalline pyridine hydrochloride by filtration, evaporation of the filtrate *in vacuo*, and recrystallization of the residue from absolute ethanol. There resulted 7·5 g (75%) of leaflets, m.p. 119–120°; showing positive tests with aqueous permanganate and bromine in carbon tetrachloride, readily hydrolyzable by means of 2% ethanolic NaOH aq. to the original acid and alcohol moieties; λ_{max} in mμ (log ε) 270 (4·21), 310 (4·42); λ_{min} 279 (4·17). (Found: C, 66·49; H, 5·63. $C_{22}H_{22}O_7$ requires: C, 66·32; H, 5·57%).

trans-3,4-*Methylenedioxycinnamyl* trans-3,4-*methylenedioxycinnamate* (Ic). Following the same procedure as for Ib there was obtained 6 g (61%) microcrystals, m.p. 122·5–123·5°; giving tests and hydrolysis as before; λ_{max} in mμ (log ε) 270 (4·22), 291 (4·24), 322 (4·30); λ_{min} 280 (4·16), 302·5 (4·23). (Found: C, 68·06; H, 4·85. $C_{20}H_{16}O_6$ requires: C, 68·18; H, 4·58%).

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[7] J. L. H. Allan, G. D. Meakins and M. C. Whiting, *J. Chem. Soc.* 1874 (1955).

[8] R. D. Haworth, W. H. Perkin and J. Rankin, *J. Chem. Soc.* **125**, 1686 (1924).

[9] E. C. Horning, J. Koo and G. N. Walker, *J. Amer. Chem. Soc.* **73**, 5826 (1951).

[10] R. D. Haworth, W. H. Perkin and T. S. Stevens, *J. Chem. Soc.* 1764 (1926).

trans-3,4-*Methylenedioxycinnamyl* trans-3,4-*dimethoxycinnamate* (Id). Following the same procedure as for Ib, there was obtained a 71% yield of fine needles, m.p. 95·5–96·5°; giving hydrolysis as before; λ_{max} in mμ (log ε) 271·5 (4·23), 295 shoulder (4·34), 320 (4·37); λ_{min} 278 (4·21). (Found: C, 68·72; H, 5·63. $C_{21}H_{20}O_6$ requires: C, 68·47; H, 5·47%).

trans-*Cinnamyl* trans-*cinnamate* (Ia). Following the same procedure as for Ib, there was obtained a 60% yield of the parent ester, m.p. 44–44·5° (lit.[3] m.p. 44°); λ_{max} in mμ (log ε) 216 (3·45), 223 (3·25), 256 shoulder (3·42), 273 (3·46); λ_{min} 222 (3·23), 230 (2·96); NMR absorptions (in $CDCl_3$) at ca. $\delta = 7{\cdot}68$ (doublet, 1 H—β to carbonyl, J = 16 c/s), 7·1–7·5 (complex—aromatic H atoms), 6·2–6·6 (complex, probably 3H; including a doublet at ca. 6·38 assigned to 1 H—α to carbonyl, J = 16 c/s), and 4·79 ppm (doublet, 2 H—methylene).

trans-*Cinnamyl phenylpropiolates*

2,3-*Dibromo*-3-(3,4,5-*trimethoxyphenyl*)*propionic acid.* To an ice-cold solution of 10 g methyl 3,4,5-trimethoxycinnamate in 50 ml chloroform was added, with stirring over a period of 30 min and until an orange-red color just persisted in the reaction mixture, a solution of ca. 2·2 ml Br_2 in 25 ml chloroform. After an additional 30 min stirring in the cold, the solvent was evaporated and the solid residue washed with petrol, yield of crude dibromo ester 13·7 g (84%), m.p. 105–108°. Recrystallization of a small sample from benzene–ligroin (60–90°) gave fine needles, m.p. 109–110°. (Found: C, 38·06; H, 4·04; Br, 38·56. $C_{13}H_{16}Br_2O_5$ requires: C, 37·88; H, 3·91; Br, 38·80%).

3,4,5-*Trimethoxyphenylpropiolic acid.* A mixture of the preceding crude dibromo ester, a saturated aq. solution of 6.4 g KOH and 40 ml absolute ethanol was refluxed 6 hr, diluted with water, acidified and refrigerated overnight. Recrystallization of the resultant precipitate from methanol and then from carbon tetrachloride gave 3·5 g (45%) needles, m.p. 140–141°, raised to 141·5–142° on recrystallization from the latter solvent. (Found: C, 61·00; H, 5·26. $C_{12}H_{12}O_5$ requires: C, 61·01; H, 5·12%).

2-*Bromo*-3-(3,4-*methylenedioxyphenyl*)*acrylic acid.* Br_2 was added to ethyl 3,4-methylenedioxycinnamate in the manner described for reaction of methyl 3,4,5-trimethoxycinnamate, except that CCl_4 was used as solvent. The residual dibromo ester was recrystallized from ligroin, m.p. 82–84°. To a solution of 21 g (excess) KOH in 100 ml 95% ethanol was added 28 g dibromo ester. The solution (spontaneously hot) was stirred (while it cooled) for 6 hr and then was allowed to stand overnight. The resultant precipitate was washed with ethanol, dissolved in 700 ml water and acidified. The precipitated acid formed cream-colored prisms from ethyl acetate, m.p. 191–192°, yield 20·5 g (quant.). (Found: C, 44·39; H, 2·74; Br, 29·51. $C_{10}H_7BrO_4$ requires: C, 44·31; H, 2·60; Br, 29·48%).

3,4-*Methylenedioxyphenylpropiolic acid.* A mixture of the preceding bromo acid (20 g), a saturated aq. solution of 21 g KOH and 100 ml absolute ethanol was refluxed and stirred for 10 hr. The residue from evaporation of the solvent was dissolved in water and acidified. The precipitated acid gave needles (8·2 g, 59%), m.p. 172–173°, on recrystallization from ethyl acetate (lit,[11] m.p. 166°).

The *methyl ester* formed yellowish needles from benzene–petrol, m.p. 79–80°. (Found: C, 64·53; H, 3·87. $C_{11}H_8O_4$ requires: C, 64·70; H, 3·95%).

trans-3,4-*Methylenedioxycinnamyl* 3,4,5-*trimethoxyphenylpropiolate* (IIIb). 3,4,5-Trimethoxyphenylpropiolic acid (3 g) was allowed to stand at room temp with 2–2·5 ml fresh reagent grade thionyl chloride until a clear solution resulted (30 min). Excess thionyl chloride was removed as for Ie. A solution of the pale yellow residue in 20 ml benzene was refluxed with a solution of 3 g 3,4-methylenedioxycinnamyl alcohol in 2·5 ml anhydrous pyridine for 5 hr and then allowed to stand overnight at room temp. The reaction mixture was processed further as for Ie to give pale brown crystals (2·2 g, 44%) from benzene–petrol, m.p. 128–130°, converted to faintly tan needles, m.p. 130–131°, on recrystallization. (Found: C, 66·78; H, 5·21. $C_{22}H_{20}O_7$ requires: C, 66·66; H, 5·09%).

trans-3,4-*Methylenedioxycinnamyl* 3,4-*dimethoxyphenylpropiolate* (IIId). Using the same procedure as for IIIb (except that it required 2 hr for the acid to dissolve in the thionyl chloride), there were obtained pale brown crystals (1·9 g, 36%) from benzene–petrol, m.p. 138–140°, converted to colorless needles, m.p. 142–143°, on recrystallization from ethyl acetate. (Found: C, 68·71; H, 5·19. $C_{21}H_{18}O_6$ requires: C, 68·84; H, 4·95%).

3,4-*Methylenedioxycinnamyl* 3-*chloro*-3-(3,4-*dimethoxyphenyl*)*acrylate* (Vd). When the preceding synthetic procedure was followed except that the thionyl chloride had been stored in a glass-stoppered bottle for 2 months, there were obtained needles of Vd, m.p. 122–123°, from benzene–petrol. (Found:

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[11] See reference 2, Vol. XIX, p. 281 (1934).

C, 62·54; H, 4·76; Cl, 8·77. $C_{21}H_{19}ClO_6$ requires: C, 62·61; H, 4·75; Cl, 8·80%). The IR spectrum of Vd (in nujol) showed a band at 1700 cm^{-1} (α,β-unsaturated ester). From the mother liquor was isolated material of m.p. 105–120°, which showed IR bands for the presence of IIId but from which we were unable to isolate IIId.

Reaction of trans-3,4-*methylenedioxycinnamyl alcohol with* 3,4-*methylenedioxyphenylpropiolic acid.* The same procedure as for IIIb was used, except that the thionyl chloride–acid mixture was allowed to stand 24 hr in order to obtain a clear solution. Crystals deposited from the cold mixture resulting from refluxing the acid chloride with the alcohol in the presence of pyridine and benzene. These crystals were separated by decantation and extracted with hot benzene. From the benzene extract were obtained crystals (1·1 g) of 3,4-*methylenedioxycinnamyl* 3-*chloro*-3-(3,4-*methylenedioxyphenyl)acrylate* (Vc), m.p. 149–155°, converted to needles, m.p. 160–161°, on recrystallization from the same solvent; IR band (nujol) at 1700 cm^{-1} (α,β-unsaturated ester). (Found: C, 62·42; H, 4·13; Cl, 9·20. $C_{20}H_{15}ClO_6$ requires: C, 62·10; H, 3·91; Cl, 9·17%).

The preceding decanted mother liquor was washed and dried as previously and evaporated. Concentration of a benzene solution of the residue gave an additional 0·2 g (21% total) of Vc. Addition of petrol to the benzene mother liquor caused deposition of more crystals, recrystallized repeatedly from benzene–petrol to give a cream-colored powder (1·4 g, 25%) of trans-3,4-*methylenedioxycinnamyl* 3,4-*methylenedioxyphenylpropiolate* (IIIc), m.p. 103–105° (104–105° for analytical sample), with sintering from 97°. (Found: C, 68·23; H, 4·21. $C_{20}H_{14}O_6$ requires: C, 68·57; H, 4·03%).

trans-*Cinnamyl* cis-*cinnamates*

Typical synthetic procedure. A solution of 0·3 g of preceding *trans*-cinnamyl phenylpropiolate in 20 ml ethyl acetate containing two drops quinoline was agitated with Lindlar catalyst[12] (0·15 g in the presence of H_2 at atm. press.). Reaction ceased after the absorption of a one molar quantity of H_2 (1–3 hr). The filtered solution was evaporated in a current of air and the residue was crystallized from a suitable solvent.

trans-3,4-*Methylenedioxycinnamyl* cis-3,4,5-*trimethoxycinnamate* (IIb). Hydrogenation of IIIb gave a liquid which crystallized from methanol–petrol as needles (76%), m.p. 86–87°; λ_{max} in mμ (log ε) 270 (4·23), 307·5 (4·35); λ_{min} 280 (4·17). (Found: C, 66·13; H, 5·53. $C_{22}H_{22}O_7$ requires: C, 66·32; H, 5·57%).

trans-3,4-*Methylenedioxycinnamyl* cis-3,4-*methylenedioxycinnamate* (IIc). Hydrogenation of IIIc gave a liquid which crystallized from methanol. Recrystallization from benzene–petrol gave prisms (43%), m.p. 66–67°; λ_{max} in mμ (log ε) 270 (4·21), 295 (4·22), 321 (4·23); λ_{min} 280 (4·16), 302 (4·21). (Found: C, 67·87; H, 4·66. $C_{20}H_{16}O_6$ requires: C, 68·18; H, 4·58%).

trans-3,4-*Methylenedioxycinnamyl* cis-3,4-*dimethoxycinnamate* (IId). Hydrogenation of IIId gave a solid which was recrystallized from methanol to give fine, slightly cream-colored needles (84%), m.p. 90–91° (depressed to 83° on admixture with the *trans-trans* ester Id); λ_{max} in mμ (log ε) 270 (4·23), 315 (4·34); λ_{min} 279 (4·19). (Found: C, 68·47; H, 5·66. $C_{21}H_{20}O_6$ requires: C, 68·47; H, 5·47%).

Phenylpropargyl trans-*cinnamate* (IV)

To a cold (−78°) solution of 0·9 g (0·023 mole) $LiAlH_4$ in 50 ml dry ether was added dropwise, with stirring, 12 g (0·1 mole) phenylpropargyl aldehyde (Aldrich Chemical Co.). After 5 min longer, water was slowly added and the mixture was allowed to warm to room temp. From the dried organic layer and ethereal extracts of the aqueous phase was obtained (on distillation) 10·4 g (88%) of liquid *phenylpropargyl alcohol*, b.p. 89–95° (0·8 mm), n_D^{23} 1·5836; IR bands (neat) at 3450 (strong, broad, OH) and 2250 cm^{-1} (medium, C≡C); lit.[13] b.p. 103–105° (1·5 mm), n_D^{18} 1·5820 from reduction of methyl phenylpropiolate.

Esterification of *trans*-cinnamic acid with phenylpropargyl alcohol was effected by the procedure used for Ib except that the second mixture was refluxed for only 4 hr. Crystallization from ethanol gave IV (65%), obtained as prisms, m.p. 53–55°, changed to 54·5–55·5° on recrystallization; λ_{max} in mμ (log ε) 218 (4·28), 224 (4·31), 243 (4·31), 279 (4·43); λ_{min} 221 (4·27), 229 (4·17), 258 (4·24); IR bands ($CHCl_3$) at 2240 (weak, C≡C), 1725 (strong, α,β-unsaturated ester), and 980 cm^{-1} (strong,

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[12] H. Lindlar, *Helv. Chim. Acta* 35, 446 (1952).

[13] E. B. Bates, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.* 1854 (1954).

trans -CH=CH-); NMR absorptions (in $CDCl_3$) at ca. $\delta = 7{\cdot}76$ (doublet, 1 H—β to carbonyl, J = 16 c/s), 7·63–7·45 (complex, ca. 10 H—aromatic), 6·51 (doublet, 1 H—α to carbonyl, J = 16 c/s), and 5·09 ppm (singlet, 2H—methylene). (Found: C, 82·43; H, 5·63; mol. wt.(Rast),[14] 245. $C_{18}H_{14}O_2$ requires: C, 82·42; H, 5·38%; mol. wt., 262).

General spectral observations on esters

Characteristic of the *trans,trans* dienic esters were UV absorption maxima at 270–271 mμ (log ε 4·22) and 310–322 mμ (log ε 4·3–4·4) and a total spectrum which was almost the exact summation of those of the corresponding ethyl *trans*-cinnamate and *trans*-3,4-methylenedioxycinnamyl alcohol. The IR spectra (in $CHCl_3$) contained strong bands at ca. 1710 (α,β-unsaturated ester), 968 (*trans* -HC=CH- in the alcohol moiety) and 980 cm^{-1} (*trans* -HC=CH- in the acid moiety).[15] The NMR spectra (in $CDCl_3$) were complex but showed a doublet for the proton on the β-carbon of the acid moiety at ca. $\delta = 7{\cdot}7$ ppm (J = 16 c/s).[16,17]

For each member of the series of *trans,cis* dienic esters the UV absorption spectrum showed a maximum at 270 mμ (ascribable largely to the common alcohol moiety) of the same intensity as in the *trans,trans*-dienic esters and another maximum at 308–321 mμ (ascribable largely to the acid moiety). Comparison of the 3 cases wherein geometric isomeric esters (I and II) were studied shows that the long wavelength absorption maximum occurs at a slightly shorter wavelength (Δ = 1–5 mμ) and has slightly decreased intensity ($\Delta \log \varepsilon$ = 0·03–0·07) in the *trans,cis* compound II.[18] The IR spectra (in $CHCl_3$) contained bands at ca. 1715 and 968 cm^{-1} (but none at ca. 980 cm^{-1}). The NMR spectrum of IId showed a singlet or close doublet ($J \leq 1$ c/s) at ca. 7·7 ppm, as compared to the highly resolved doublet in the *trans,trans* isomers.[17]

The *trans*-cinnamyl phenylpropiolates showed strong IR absorption bands at 2220–2240 (-C≡C-) and 1690–1710 cm^{-1} (α,β-unsaturated ester).

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[14] Determined by Clark Microanalytical Laboratory, Urbana, Illinois.

[15] L. J. Bellamy, *The Infra-red Spectra of Complex Molecules* pp. 45–49, 178–187. Methuen, London (1958).

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