

Studies on the Raman Effect of Organic Substances. VIII. Raman Effect of Furane Derivatives.

By Kichimatsu MATSUNO and Kwan HAN.

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Introduction. In our two previous papers,⁽¹⁾⁽²⁾ investigations on the Raman spectra of ethyl cinnamate and ethyl α -furfuracrylate were described. In the present investigation, the Raman spectra of methyl and ethyl esters of the so-called stable α -furfuracrylic acid, *trans*-cinnamic acid, and the reduced products, viz., α -furylpropionates and hydrocinnamates, have been taken, in order to study the relation between the Raman spectra and the isomerism.

Experimental. The substances used were synthesized by the following processes: Methyl α -furfuracrylate (I) (m.p. 26.5°, b.p. 96°/3 mm.) and ethyl α -furfuracrylate (II) (b.p. 114°/3 mm.) were prepared by treating the mixtures of the silver salt of stable α -furfuracrylic acid, F-CH:CH-COOH* (m.p. 140°) and the corresponding alkyl iodides.


trans-Methyl cinnamate (III) (m.p. 34°, b.p. 127°/10 mm.) and *trans*-ethyl cinnamate (IV) (b.p. 136°/10 mm.) were obtained by treating Kahlbaum's cinnamic acid (m.p. 133°) and the corresponding alcohols in the presence of concentrated sulphuric acid, according to the method of Fischer and Speier.⁽³⁾

Methyl α -furylpropionate (V) (b.p. 67°/3 mm.) and ethyl α -furylpropionate (VI) (b.p. 74°/8 mm.) were obtained by reducing the corresponding α -furfuracrylate, F-CH:CH-COOR, with 2.5% sodium amalgam in alcohol solution in the presence of acetic acid. The reduction was repeated until the intense Raman line at $\Delta\nu$ 1640 cm.⁻¹ in the Raman spectra, associated with the C:C bond, disappeared.

Methyl hydrocinnamate⁽⁴⁾ (VII) (b.p. 105°/8 mm.) and ethyl hydrocinnamate⁽⁴⁾ (VIII) (b.p. 127°/15 mm.) were prepared by warming the

(1) This Bulletin, **9** (1934), 88.

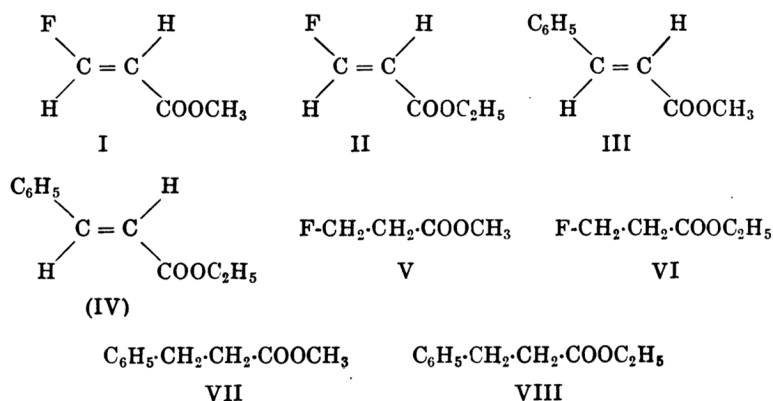
(2) *Ibid.*, **9** (1934), 327.

* F denotes α -furyl group  in this paper.

(3) Fischer and Speier, *Ber.*, **28** (1895), 3254.

(4) Erlenmeyer, *Ann.*, **137** (1866), 334.

mixtures of hydrocinnamic acid (m.p. 48°) and the corresponding alcohols by the action of dry hydrogen chloride. All the substances were washed with the solution of sodium bicarbonate or sodium carbonate and finally with water. After dehydrating over calcium chloride and sucking off all the ether, the esters were distilled under reduced pressure. The middle fraction in the final distillation was employed in the investigation. The structural formulæ of the substances are as follows:



trans-Methyl cinnamate (m.p. 34°) is colourless crystals at room temperature, while *cis*-methyl cinnamate being a liquid (m.p. -3.5°) which agrees with the results obtained by Kistiakowsky and his co-worker.⁽⁵⁾ The so-called stable methyl α -furfuracrylate is also colourless crystals (m.p. 26.5°). The ether solution (ca. 1/5 mol) of methyl furfuracrylate and methyl cinnamate were used in the experiments of the Raman spectra. After long exposure the solvent was removed off and the crystals identical with the *trans*-methyl cinnamate and methyl α -furfuracrylate were recovered.

The Raman spectra were taken by means of a spectrograph with three prisms,⁽²⁾ using a saturated solution of sodium nitrite as a filter, in order to prevent the samples from the isomerization due to the action of the light in ultra-violet region. The numbers of the Raman lines (n), the numbers of the plates, and the conditions under which the spectra were taken, are summarized in Table 1. The results of the Raman spectra are shown in Table 2. Methyl cinnamate in the fused state and ethyl cinnamate have been studied by Kohlrausch and his co-worker.⁽⁶⁾ The results are compared in Table 3.

(5) G. B. Kistiakowsky and Walter R. Smith, *J. Am. Chem. Soc.*, **57** (1935), 269.

(6) K. W. F. Kohlrausch and A. Pongratz, *Monatsh.*, **64** (1934), 374.

Table 1.

Substance	<i>n</i>	No. of plates	Width of slit (10 ⁻² mm.)	Temp. (°C.)	Time of exposure (hours)
Methyl α -furfuracrylate (I)	20	365	65	15	8
Ethyl α -furfuracrylate (II)	32	372	55	15	14
<i>trans</i> -Methyl cinnamate (III)	59	356	65	22	14
<i>trans</i> -Ethyl cinnamate (IV)	65	354	65	23	6
Methyl α -furylpropionate (V)	33	360	60	22	8
		361	65	21	14
Ethyl α -furylpropionate (VI)	23	366	65	15	8
Methyl hydrocinnamate (VII)	27	363	65	20	12
Ethyl hydrocinnamate (VIII)	25	359	65	23	8

Table 2. The $\bar{\nu}$ Values of the Raman Spectra of Furane Derivatives.(1) Methyl α -Furfuracrylate (I).

135 (2d); 384 ($1\frac{1}{2}$ d); 776 (4); 887 (2); 930 (1); 1023 (6); 1081 (3); 1160 (5); 1217 (5); 1268 (4); 1237 (5); 1396 (6); 1441 (2); 1485 (8); 1574 (2); 1644 (10); 1715 (5d); 3130 (3).

(2) Ethyl α -furfuracrylate (II).

761 (2); 794 (2); 817 (1); 862 (1); 887 (3); 934 (4); 978 (1d); 1021 (8); 1082 (4); 1160 (6); 1190 (2); 1212 (6); 1265 (5); 1283 (8); 1311 ($1\frac{1}{2}$); 1334 ($1\frac{1}{2}$); 1361 (1); 1389 (9); 1478 (10); 1575 (3); 1642 (10); 1704 (8d); 2928 (1d); 2976 (2); 3121 (2); 3151 ($1\frac{1}{2}$).

(3) *trans*-Methyl cinnamate (III).

216 (1b, d); 360 ($1\frac{1}{2}$); 576 (2); 616 (4); 718 (4); 769 (1d); 834 (3b); 861 (3); 933 (2b); 998 (8); 1028 (2b); 1158 (6b); 1179 (6b); 1201 (5); 1267 (4b, d); 1307 (3b, d); 1335 (2); 1443 (5d); 1494 (4); 1574 (4); 1597 (9b); 1634 (10b); 1713 (6b); 2841 (2b, d); 2875 (3b, d); 2963 (3); 3058 (1b, d).

(4) *trans*-Ethyl cinnamate (IV).

177 (2b, d); 279 (1b, d); 403 (2d); 475 (0); 571 (4); 616 (6s); 717 (4b, d); 740 (2); 775 (3); 836 (5); 867 (5d); 977 (1d); 996 (10s); 1025 (3); 1116 (3b, d); 1156 (3); 1178 (8); 1200 (8); 1259 (6d); 1303 (5d); 1331 (3); 1363 (3); 1392 (3); 1447 (5); 1494 (5); 1572 (3); 1597 (10); 1634 (10); 1706 (8); 2922 (3d); 2981 (3); 3067 (5d).

Table 2.—(Concluded)

(5) Methyl α -furylpropionate (V).

384 ($1/2$ d); 700 ($1/2$); 837 (1); 886 (2); 922 ($1/2$ d); 1019 (2); 1054 (1); 1078 (5); 1145 (4b, d); 1215 (3); 1388 (5); 1450 (1b, d); 1508 (10); 1599 (5); 1735 (2d); 2924 (2d); 2954 (3); 3118 (5); 3155 (2).

(6) Ethyl α -furylpropionate (VI).

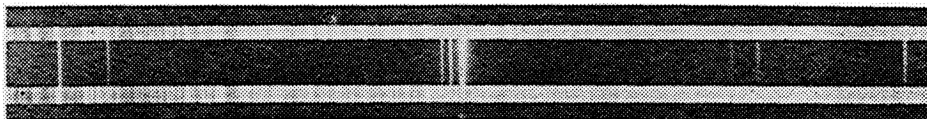
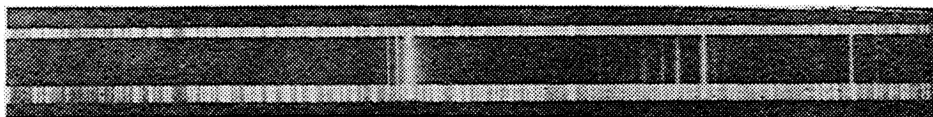
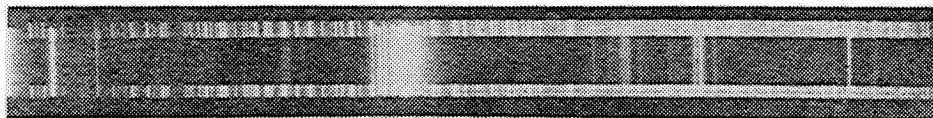
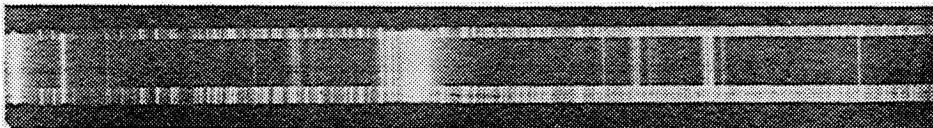
699 ($1/2$); 858 (2); 882 (2); 922 ($1/2$); 1017 (1); 1050 ($1/2$); 1079 (4); 1118 ($1/2$); 1143 (2b); 1213 (3); 1387 (3); 1451 (2d); 1505 (8); 1597 (5); 1734 (2d); 2929 (3d); 2983 (2); 3126 (2); (3154) (3).

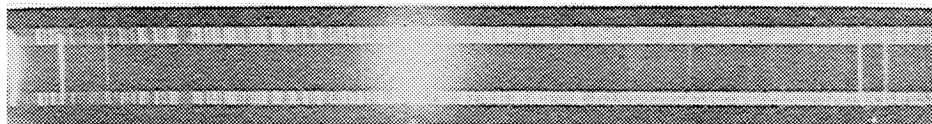
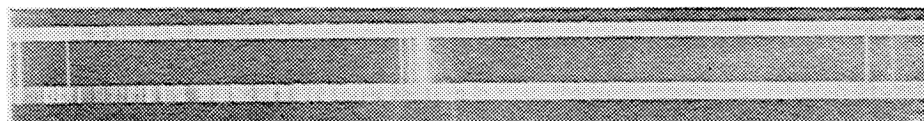
(7) Methyl hydrocinnamate (VII).

244 (2d); 424 (2d); 618 (5); 749 (1d); 759 (3); 837 (1d); 889 (3); 941 (2b); 997 (10); 1025 (5); 1178 (2); 1197 (5); 1443 (2d); 1578 (2); 1597 (6); 1630 (2); 1730 (3d); 2841 (1); 2917 (3b); 2945 (2d); 2997 (2); 3053 (3d).

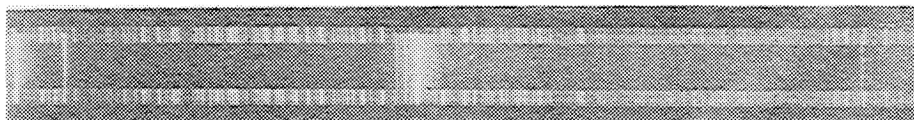
(8) Ethyl hydrocinnamate (VIII).

374 ($1/2$); 618 (3); 767 (2); 859 (1); 999 (8); 1028 (4); 1105 (2d); 1174 (3); 1196 (6); 1261 (5); 1446 (2); 1589 (1); 1602 (6); 1724 (3d); 2926 (2d); 2970 (1); 3056 (5d).

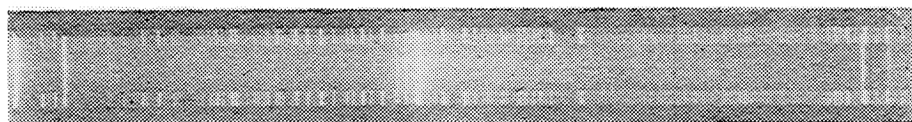
(1) Methyl α -furfuracrylate (I)(2) Ethyl α -furfuracrylate (II)(3) *trans*-Methyl cinnamate (III)(4) *trans*-Ethyl cinnamate (IV)

(5) Methyl α -furylpropionate (V)(6) Ethyl α -furylpropionate (VI)

(7) Methyl hydrocinnamate (VII)



(8) Ethyl hydrocinnamate (VIII)



Discussion. In the previous papers,⁽¹⁾⁽²⁾ one of the authors has shown that the Raman frequencies, ω_1 626, ω_2 885, ω_3 923, ω_4 1018, ω_5 1083, ω_6 1150, ω_7 1223, ω_8 1384, ω_9 1505, ω_{10} 1602, ω_{11} 3117, and ω_{12} 3150 cm^{-1} are characteristic of the α -furfuryl-compounds, and the frequencies in the region between $\Delta\nu$ 1460 and 1600 cm^{-1} can be used as an indicator to distinguish α -furfuryl- from α -furfuridene or α -furoyl-compounds. In the present investigation, the frequencies of $\Delta\nu$ 1478, 1575, and 1642 cm^{-1} are found in α -furfuracrylates while 1505 and 1597 cm^{-1} are found in α -furylpropionates, as shown in Table 4. The appearance of $\Delta\nu$ 1642 cm^{-1} in the former but not in the latter cases is reasonable, for the appearance of a Raman shift, $\Delta\nu$ 1640 \pm 20 is quite indicative of a double linkage in the side chain.

It has been observed that there is a considerable difference between the spectra of the *cis*- and *trans*-isomers.⁽⁷⁾ Grédy⁽⁸⁾ has investigated the Raman spectra of the *cis-trans*-isomers of cinnamic compounds and concluded that 1264, 1408, 1642, and 3021 cm^{-1} are found in the

(7) H. Hibben, *Chem. Rev.*, **18** (1936), 31.

(8) Blanche Grédy, *Compt. rend.*, **202** (1936), 664.

Table 3. Comparison of the Results on Cinnamates.

Methyl cinnamate		Ethyl cinnamate	
Kohlrausch	The authors	Kohlrausch	The authors
217	216	—	177
274	—	—	279
357	360	—	403
402	—	—	475
576	576	582	571
616	616	616	616
710	718	718	717
—	—	—	740
771	769	—	775
837	834	846	836
862	861	865	867
938	933	—	—
977	—	—	977
998	998	1004	996
1028	1028	1030	1025
—	—	—	1116
1165	1158	1163	1156
1181	1179	1185	1178
1201	1201	1201	1200
1268	1267	1264	1259
1311	1306	1303	1303
1336	1335	1324	1331
—	—	—	1363
—	—	—	1392
1447	1443	1446	1447
1495	1494	1496	1494
1578	1574	—	1572
1598	1597	1595	1597
1634	1634	1631	1634
1712	1713	1706	1706
2836	2841	—	—
2880	2875	2934	2922
2956	2963	2980	2981
3037	3058	3055	3067

Table 4.

C ₆ H ₅ ·CH : CH·COOR		F·CH : CH·COOR		F·CH ₂ ·CH ₂ ·COOR	
R = CH ₃	R = C ₂ H ₅	R = CH ₃	R = C ₂ H ₅	R = CH ₃	R = C ₂ H ₅
718	717	—	—	700	699
—	740	—	—	—	—
769	775	776	761	—	—
—	—	—	794	—	—
834	836	—	817	837	—
861	867	—	862	—	858
—	—	887	887	886	882
933	977	930	934	922	922
—	—	—	978	—	—
998	996	—	—	—	—
1028	1025	1023	1021	1019	1017
—	—	—	—	1054	1050
—	1116	1081	1082	1078	1079
1158	1156	—	—	—	1118
1179	1178	1160	1160	1145	1143
1201	1200	—	1190	—	—
1267	1259	1217	1212	1215	1213
1306	1303	1268	1265	—	—
—	—	1287	1283	—	—
1335	1331	—	1311	—	—
—	1363	—	1334	—	—
—	1392	—	1361	—	—
1443	1447	1396	1389	1388	1387
1494	1494	1441	—	1450	1451
1572	1572	1485	1478	1508	1505
1597	1597	1574	1575	—	—
1634	1634	—	—	1599	1597
1713	1706	1644	1642	—	—
—	—	1715	1704	1735	1734

cis-forms, while 1209, 1274, and 1657 cm.⁻¹ in the *trans*-forms as shown in Table 5. The disappearance of $\Delta\nu$ 1408 and the appearance of 1201, 1306, and 1634 in the *trans*-cinnamates may give an evidence that a little transition from *cis*- to *trans*-forms takes place during the experiment of the Raman spectra under the filtered mercury light. It is likewise

possible to consider that the disappearance of 1408 and the appearance of 1190, 1212,⁽⁹⁾ 1283, and 1642 cm.⁻¹ in furfuracrylates are attributable to the *trans*-forms of the esters.

Table 5. Some Raman shifts in the *cis*- and *trans*-isomers of cinnamic compounds observed by Grédy.⁽⁸⁾

$C_6H_5 \cdot CH : CH \cdot CH_3$	$\begin{cases} cis \\ trans \end{cases}$	1210	$\begin{matrix} 1264 \\ 1278 \end{matrix}$	1408	$\begin{matrix} 1642 \\ 1665 \end{matrix}$	3021
$C_6H_5 \cdot CH : CH \cdot CH_2OH$	$\begin{cases} cis \\ trans \end{cases}$	1209	$\begin{matrix} 1256 \\ 1274 \end{matrix}$	1408	$\begin{matrix} 1642 \\ 1657 \end{matrix}$	3022
$C_6H_5 \cdot CH : CH \cdot CH_2OCH_3$	$\begin{cases} cis \\ trans \end{cases}$	1208	$\begin{matrix} 1255 \\ 1278 \end{matrix}$	1410	$\begin{matrix} 1643 \\ 1657 \end{matrix}$	3025
$C_6H_5 \cdot CH : CH \cdot CH_2OCOCH_3$	$\begin{cases} cis \\ trans \end{cases}$		$\begin{matrix} 1250 \\ 1281 \end{matrix}$	1412	$\begin{matrix} 1645 \\ 1659 \end{matrix}$	3032
$C_6H_5 \cdot CH : CH \cdot CH_2Br$	<i>trans</i>	1206	1282		1646	

It is doubtful, at a glance, that the important Raman shift associated with the C:C linkage has the values of $\Delta\nu$ 1634 in *trans*-cinnamates and 1642 cm.⁻¹ in α -furfuracrylates. But it is reasonable to consider that the shift questioned above is due to the effect of a conjugated double bond of carbonyl group, C:O. It is well-known that the C:C frequency is decreased by the effect of the conjugated double bonds. We may consider some other examples from the work of Hibben.⁽⁷⁾

Table 6. The Effect of Substitution on the C:C Shifts.

Radical R	$CH_2 : CH \cdot R$	$R \cdot CH : CH \cdot R$	
		<i>cis</i>	<i>trans</i>
CH_3	1647		
CH_2OH	1646	1658	1677
C_nH_{2n+1} ($n = 2-6$)	1642	1658	1674
C_6H_5	1631	1642	1665
$COOH$	1638	1645	1652
$COOR$		1644	1655
CHO	1618	1625	1642
CN		1628	1645

(9) $\Delta\nu$ 1212 cm.⁻¹ is also attributable to the furane ring.

It is obvious that the carbonyl or the aromatic radical has an effect to decrease the C:C shift on account of the conjugated double bonds. Consequently, a remarkable decrease of the C:C shift will be expected in cinnamates and α -furfuracrylates which have the aromatic and the carbonyl radicals attached to the two sides of the ethylene linkage. The fact that $\Delta\nu$ 1634 cm.⁻¹ was found in stilbene⁽¹⁰⁾ and $\Delta\nu$ 1640 cm.⁻¹ in diethyl fumarate⁽¹¹⁾ seems to make an other confirmation about it. If the *cis*- and *trans*-isomers were co-existent, other Raman lines, associated with the *cis*-compound, would be found at ca. $\Delta\nu$ 1620–1630 cm.⁻¹ besides the shift mentioned above. We may consider that the appearance of the intense lines at $\Delta\nu$ 1634 cm.⁻¹ in cinnamates and at $\Delta\nu$ 1642 cm.⁻¹ in the so-called stable α -furfuracrylates is attributable to the *trans*-form of the substances.

Summary.

(1) The Raman spectra of methyl and ethyl esters of α -furfuracrylic acid, cinnamic acid, α -furylpropionic acid, and hydrocinnamic acid have been measured.

(2) On comparing the Raman spectra of α -furfuracrylates with those of *trans*-cinnamates and other cinnamic compounds, the so-called stable furfuracrylates are considered as the *trans*-esters.

In conclusion, the authors are indebted to Ass. Prof. T. Nozoe for his valuable advice in the work of synthesis of the samples. The expense of this experiment was paid from a grant given by the Nippon Gakuzyutu Sinko Kwai, for which thanks are due.

*Laboratory of Physical and Inorganic Chemistry,
Taihoku Imperial University, Taihoku.*

(10) Dadiou, Pongratz, and Kohlrausch, *Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse, Abt. II a*, **140** (1931), 353.

(11) Dadiou, Pongratz, and Kohlrausch, *ibid.*, **140** (1931), 647.