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A comparative vibrational and NMR study of *cis*-cinnamic acid polymorphs and *trans*-cinnamic acid

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Abstract

The IR and Raman spectra of the two polymorphic forms (58°- and 68°-forms) of *cis*-cinnamic acid were measured, and the spectral differences discussed on the basis of the crystal structures of the two forms. The IR bands related to the COOH group differ in the frequencies and band shape, reflecting differences in the hydrogen bonding between the two modifications. These spectra were compared with those of *trans*-cinnamic acid. The IR, Raman, and NMR spectra of the isotopic compounds, including the deuterated and ^{13}C analogs of the cis and trans acids, were also recorded in the solid state and in solution to confirm the spectral assignments.

Keywords: *cis*-Cinnamic acid; *trans*-Cinnamic acid; Polymorphism; IR/Raman spectra; NMR spectra

1. Introduction

cis-Cinnamic acid (*cis*-CA) (allocinnamic acid, *Z*-3-phenyl-2-propenoic acid) is known to have the four polymorphic forms (mps 68, 58, 42, and 32°C), and their characteristics have been investigated by many authors, as seen in Beilstein Handbook [1–4]. The polymorphism of cinnamic acids and their IR and Raman spectra were discussed by Guy et al. [5–8]; however, the problem of how to explain the observed spectral differences remained unresolved from lack of X-ray studies. In earlier studies [9,10], we reported the X-ray structures of the two modifications (mps 68 and 58°C) of *cis*-cinnamic acid; the major structural difference between the two polymorphs

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was found in the C(phenyl)–C(olefinic) torsion angle. The present paper deals with the characterization of the polymorphs of *cis*-CA by vibrational and NMR spectra on the basis of the crystal structure and with the assignment of the solution spectra. The spectra of *trans*-cinnamic acid (*trans*-CA) (*E*-3-phenyl-2-propenoic acid) are also reported for comparison.

2. Experimental

2.1. Materials

The method of preparing the two polymorphs (the 58°- and 68°-forms) of *cis*-CA was described in previous papers [9,10]. The purity of these samples was checked by elemental analyses and NMR spectra. Attempts to obtain the third and fourth forms (the 42 and 32° acids) were unsuccessful.

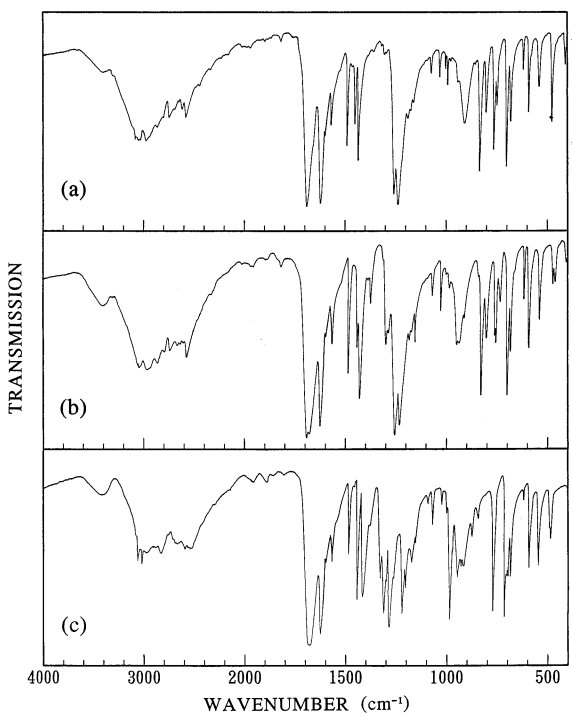

Fig. 1. IR spectra of *cis*- and *trans*-cinnamic acids in the solid state: (a) *cis*-CA, 58°-form; (b) *cis*-CA, 68°-form; and (c) *trans*-CA.

The two isotopic compounds, *cis*-CA-2-^{13}C and *cis*-CA-3-^{13}C, were prepared to establish the assignment of the ^{13}C NMR spectra. The ^{13}C-labelled trans compounds described below were irradiated with a 400 W high-pressure mercury lamp [11]. The cis isomers were separated from the unchanged trans isomers by a difference in solubility in water and recrystallized from hexane. These samples still contained 11–16 and 14–18% of the trans isomers, respectively, as estimated by ^{1}H NMR spectra, but this did not interfere with the peak assignment.

trans-CA was obtained commercially or prepared in the preliminary experiments for obtaining the following isotopic compounds and recrystallized from water; m.p. 134°C. *trans*-CA-2-^{13}C and *trans*-CA-3-^{13}C were prepared from benzaldehyde and malonic-2-^{13}C acid (ISOTEC, Inc., 99 at.%) [12], and benzaldehyde-α-^{13}C (ISOTEC, Inc., 99.4 at.%) and acetic anhydride/sodium acetate [13], respectively; m.p. 134°C. Crystals of *trans*-cinnamic acid usually consist of the stable α-form, but may be mixtures of the stable α- and metastable β-forms. Therefore, the solid state spectra were measured for the samples annealed at 65°C for 5 h [14].

The COOD compounds were prepared by exchange reaction with D_2O to assign the OH bands.

2.2. Spectra

IR spectra of KBr discs, Nujol mulls, and $CHCl_3$ solutions were measured on Perkin-Elmer 1720X and 1640 FT-IR spectrometers and Raman spectra on Spex Ramalog-9 (excitation line: 514.5 nm from an argon ion laser) and Perkin-Elmer 2000R FT-Raman (excitation line: 1064 nm from a Spectron Laser System SL 300 Nd:YAG laser) spectrometers.

^{1}H and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded on a JEOL JNM-EX-400 spectrometer (400 MHz) using standard pulse sequences and tetramethylsilane as an internal reference. ^{13}C NMR spectral measurements of the solid samples were carried out on a JEOL JNM-GSX-400 spectrometer according to the method described in our earlier studies [9,10].

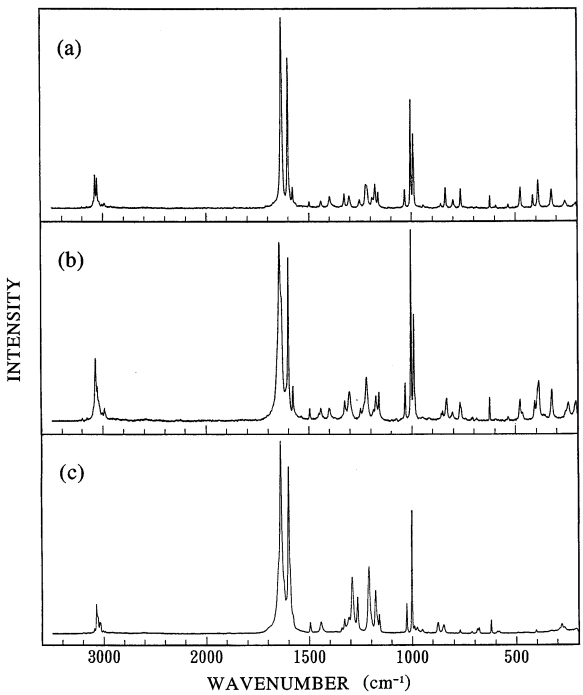

Fig. 2. Raman spectra of *cis*- and *trans*-cinnamic acids in the solid state: (a) *cis*-CA, 58°-form; (b) *cis*-CA, 68°-form; and (c) *trans*-CA.

3. Results and discussion

3.1. Spectra in the solid state

Figs. 1 and 2 show the IR and Raman spectra, respectively, of the 58 and 68° forms of *cis*-CA, and *trans*-CA. Tables 1 and 2 list some selected vibrational frequencies and assignments for these acids. Guy et al. [5–8] reported the IR and Raman spectra of the three forms of *cis*-CA and the two forms of *trans*-CA. However, their spectra are poor in resolution and considerably different from ours.

In the IR spectra, splitting of more bands is observed for the 68° acid than for the 58° acid. Although the crystal symmetry is the same (C_{2h}^5) for the two acids, the 68° crystal contains the eight molecules which have two types of configurations in the unit cell, and the 58° crystal has the four molecules which consist of the two centrosymmetrical hydrogen-bonding dimers [9,10]. The spectral differences arise from these crystal differences. The most prominent features in the IR spectra are found for the bands related to the COOH group, reflecting a difference in the structure of hydrogen bonding; the O···O distance (2.666 Å) of the 58° acid is longer than those (2.629 and 2.643 Å) of the 68° acid, and the C=O and C–O bond lengths are also different [9,10]. The 68° acid shows a doublet around 1690 cm^{-1} for the C=O stretching vibration, while the 58° acid shows a singlet at 1696 cm^{-1}. The OH out-of-plane bands differ in frequencies and band shape. That of the 68° crystal is observed as a doublet around 940 cm^{-1} and that of the 58° crystal as a singlet at 904 cm^{-1}. On the other hand, the OH in-plane bending and C–O stretching bands are not so different between the two forms.

The Raman spectra of the two crystal modifications also differ from each other, although the band splitting is not so distinct as in the IR spectra. The apparent features in the Raman spectra are observed for the C=C stretching band; the two bands are found at 1641 (strong) and 1634 cm^{-1} (shoulder) for the 68° acid. The corresponding IR band is not split, but probably the higher frequency component overlaps with the left envelope of the 1630 cm^{-1} band. For the 58° acid, the C=C bands are observed at 1631 (Raman) and 1626 cm^{-1} (IR) as in-phase and out-of-phase stretching vibrations of the symmetrical dimer, respectively. In the Raman spectra, the carboxyl C=O stretching band is very weak and concealed under the left side of the C=C bands.

The two crystal forms (α and β) are known for *trans*-CA [14,15]. The α-crystal consists of the centrosymmetrical dimer by the hydrogen bonds of the carboxylic acid groups [15–18]. The crystal structure of the β-form has not been determined owing to its instability, although the crystallographic constants have been reported [15]. The β-form is so unstable as to be transformed into the α-form on grinding in a mortar [14]. We unexpectedly obtained the *trans*-CA-2-^{13}C crystals which seemed to be those of the β-form and observed spectroscopically this phenomenon; the IR spectrum of this sample was slightly different from that of the α-form, but that of the sample

Table 1
Some vibrational frequencies (cm^{-1}) for *cis*-cinnamic acid[a]

Solid				$CHCl_3$ soln.		Assignment
58°-form		68°-form		IR	Raman	
IR	Raman	IR	Raman			
				3517 w	–	OH stretch (monomer)
2974–2572 ms, br	–	2962–2572 ms, br	–	3000–2575 ms, br	–	OH stretch (dimer)
1696 vs	–	1696 vs 1680 vs	–	1699 [4,4] vs	–	C=O stretch
1626 ms	1631 vs	1630 s	1641 vs 1634 sh	1631 [23,26] s	1632 [24,21] s	C=C stretch
1438 s	1439 vw	1434 ms	1440 vw	1436 [5,7] ms	–	OH i.p. bend[b], CH bend
1256 s or 1236 vs	1252 vw or 1222 w	1252 vs or 1230 s	1247 vw or 1219 w	1250 [1,1] s	–	C–O stretch[b]
904 m	–	949 m 937 m	–	929 [1,1] m	–	OH o.p. bend

[a] s, strong; m, medium; w, weak; v, very; br, broad; –, not observed or extremely weak; i.p., in-plane; o.p., out-of-plane. The values in brackets are the isotope shifts to lower frequencies on the 2-^{13}C and 3-^{13}C substitutions, respectively.
[b] Vibrations coupled with each other.

Table 2
Some vibrational frequencies (cm^{-1}) for *trans*-cinnamic acid[a]

Solid		$CHCl_3$ soln.		Assignment
IR	Raman	IR	Raman	
		3526 w	–	OH stretch (monomer)
2985–2542 ms,br	–	3000–2591 ms,br	–	OH stretch (dimer)
1685 [5,0] vs	–	1691 [4,2] vs	–	C=O stretch
1630 [20,22] s	1637 [17,17] vs	1634 [22,24] s	1637 [22,23] vs	C=C stretch
1422 [3,1] ms	–	1416 [2,3] ms	–	OH i.p. bend[b]
1286 [2,4] s	1292 [3,4] w	1285 [2,3] ms	–	C–O stretch[b]
944 [11,1] m	–	943 [11,1] m	–	OH o.p. bend

[a] s, strong; m, medium; w, weak; v, very; br, broad; –, not observed or extremely weak; i.p., in-plane; o.p., out-of-plane. The values in brackets are the isotope shifts to lower frequencies on the 2-^{13}C and 3-^{13}C substitutions, respectively.
[b] Vibrations coupled with each other.

which was sufficiently ground in advance was identical with the α-form spectrum.

The C=O stretching and the C–O stretching frequency (or the C–O stretching coupled with the OH in-plane bending vibration) differ between *cis*-CA and *trans*-CA, reflecting a difference in the strength of the hydrogen bond. The *cis*-58° acid shows higher C=O and lower C–O frequencies than the trans acid. For the 68° acid also, the average value of the C=O doublet is slightly higher than the frequency of the trans acid. The *trans*-CA dimer formed by hydrogen bonding is nearly planar as a whole in the crystal [16–18], whereas the cis acids are not [9,10]. The C=O and

C–O bond lengths and the O···O intermolecular distances also decrease or increase in the order of the *cis*-58° and *cis*-68°, and trans acids. It is expected from these structures that the hydrogen bond of the trans compound is stronger than that of the cis compounds.

The OH in-plane deformation band is observed at 1422 cm^{-1} for *trans*-CA and disappears on *O*-deuteration. However, the band at 1438 cm^{-1} for *cis*-CA remains unchanged on deuteration. Since the in-plane CH deformation vibration of the *cis* –CH=CH– group is known to appear in this region, the weak OH band is probably obscured owing to overlapping with the strong CH deformation band.

For the trans compound, the C=C stretching band is shifted by about 20 cm^{-1} to a lower frequency on ^{13}C-substitution. The OH out-of-plane bending band is significantly shifted in the 2-^{13}C acid, while the corresponding band of the 3-^{13}C acid is at the same frequency as the ordinary compound. This finding suggests that the movement of the 2-^{13}C atom contributes to the OH vibration.

The solid state ^{13}C NMR spectra of the cis acids were already discussed in combination with the results of X-ray analysis in our previous papers [9,10]. The chemical shifts are listed together with the solution data in Table 3. Assignment of the C(2) and C(3) signals was confirmed by the NMR measurement of the ^{13}C isotopic compounds. In these spectra, the peak splitting is characteristic of the 68° acid; the signals due to the carbons C(2), C(3), and C(4) are doublets. On the other hand, no splitting is observed for the *cis*-58° acid and *trans*-CA. The ^{13}C NMR chemical shifts for α-*trans*-CA are summarized in Table 4 together with the solution data. All the ^{13}C NMR signals in the solid state are assigned to a single molecular species consistent with the X-ray results [15–18].

Table 3
^{13}C NMR chemical shifts (ppm) for *cis*-cinnamic acids[a]

cis-CA[b]			*cis*-CA-2-^{13}C[c]	*cis*-CA-3-^{13}C[c]	Assignment
Solid		$CDCl_3$ soln.	$CDCl_3$ soln.	$CDCl_3$ soln.	
58°-acid	68°-acid				
172.8	172.9	171.41[d]	171.46 d[e]	171.46	C(1)(COOH)
150.8		145.89	145.88 d[f]	**145.89**	C(3)
	149.6				
134.2	136.7	134.38	134.38	134.36 d[h]	C(4)
	135.2				
131.1	129.9	129.97	129.97 d[g]	129.98	C(5)
129.6	128.8	129.4	129.4	129.4	C (7)
		128.1	128.1	128.10 d[i]	C (6)
117.6	120.5	118.68	**118.69**	118.66 d[f]	C(2)
	117.9				

[a] d, doublet.
[b] In the previous studies [5–8].
[c] Boldface indicates the main peaks with satellites. The other signals are observed in the expanded spectra.
[d] $^3J_{C(1)H(3)}$: 14 Hz (a doublet in the spectra recorded by a gated decoupling mode).
[e] $^1J_{C(1)C(2)}$: 72.5 Hz.
[f] $^1J_{C(2)C(3)}$: 71 Hz.
[g] $^3J_{C(2)C(5)}$: 3.7 Hz.
[h] $^1J_{C(3)C(4)}$: 55 Hz.
[i] $^3J_{C(3)C(6)}$: 3.7 Hz.

Table 4
^{13}C NMR chemical shifts (ppm) for *trans*-cinnamic acids[a]

trans-CA		*trans*-CA-2-^{13}C		*trans*-CA-3-^{13}C		Assignment
Solid	$CDCl_3$ soln.	Solid	$CDCl_3$ soln.	Solid	$CDCl_3$ soln.	
173.5	172.60[b]		172.51 d[c]		172.57	C(1)(COOH)
147.1	147.14		147.11 d[d]	147.1	**147.13**	C(3)
134.4	134.04		134.09		134.03 d[f]	C(4)
132.1	130.77		130.76		130.78	C(7)
130.2	128.98		128.99		128.98 d[g]	C(6)
128.4	128.39		128.39 d[e]		128.38	C(5)
119.7	117.33	119.6	**117.35**		117.30 d[d]	C(2)

[a] See footnotes a and c in Table 3.
[b] $^3J_{C(1)H(3)}$: 7.4 Hz (a doublet in the spectrum recorded by a gated decoupling mode).
[c] $^1J_{C(1)C(2)}$: 74 Hz.
[d] $^1J_{C(2)C(3)}$: 70 Hz.
[e] $^3J_{C(2)C(5)}$: 5.5 Hz.
[f] $^1J_{C(3)C(4)}$: 55 Hz.
[g] $^3J_{C(3)C(6)}$: 5.5 Hz.

3.2. Solution spectra

Hirota and Urushibara [19] reported that the UV spectra of the three polymorphic forms of *cis*-CA are almost the same in ethanol. Molecules in solutions are in the field of some mean intermolecular interaction which is different from crystal field; consequently, they should give the same spectra irrespective of polymorphic forms. The $CHCl_3$ solutions of both forms of *cis*-CA give identical IR and Raman spectra. The cis acid is present mostly as a dimer in $CHCl_3$ solutions, although a small amount of the monomer coexists. The OH out-of-plane bending bands in these $CHCl_3$ solutions show a frequency intermediate between those in the solid state spectra of the two forms, as seen from Table 1. On the other hand, the trans acid has the same frequencies for this vibration in the solid state and in solution. These observations suggest that the hydrogen bond structure of the cis acid in $CHCl_3$ solution is a little different from that in the solid state, whereas *trans*-CA takes the same structure in the two states.

The ^1H and ^{13}C NMR spectra of *cis*-CA in $CDCl_3$ are also identical for the two polymorphic crystals. The expected splitting is observed for the isotopic compounds as in Tables 3–6. The NMR spectra of the 1-^{13}C-labelled compounds of *cis*- and *trans*-CA were reported and the coupling constants were discussed by Chaloner [20]. For the benzene ring of the cis compound, a peak at 134.38 ppm is easily assignable to C(4) from a large coupling constant (55 Hz) in the spectrum of *cis*-CA-3-^{13}C. The C(5) and C(6) peaks are assigned as follows. A peak at 128.10 ppm is a doublet with a coupling constant 3.7 Hz in the *cis*-CA-3-^{13}C spectrum. The carbon–carbon coupling constants $^3J_{CC}$ values are known to be larger

Table 5
^1H NMR chemical shifts (ppm) for *cis*-cinnamic acids in $CDCl_3$ solution[a]

cis-CA	*cis*-CA-2-^{13}C	*cis*-CA-3-^{13}C	Assignment[b]
7.607–7.582 m	7.612–7.588 m	7.607–7.587 m	H(5)
7.358–7.340 m	7.363–7.345 m	7.363–7.345 m	H(6), H(7)
7.063 d[c]	7.068 d[c]	7.067 q[e]	H(3)
5.960 d[c]	5.963 q[d]	5.965 q[f]	H(2)

[a] d, doublet; q, quartet; m, multiplet.
[b] The numbers denote the carbon atom positions where the hydrogen atoms are attached.
[c] $^3J_{H(2)H(3)}$: 12.7 Hz.
[d] $^3J_{H(2)H(3)}$: 12.7 Hz; $^1J_{H(2)C(2)}$: 164 Hz.
[e] $^3J_{H(2)H(3)}$: 12.7 Hz; $^1J_{H(3)C(3)}$: 154 Hz.
[f] $^3J_{H(2)H(3)}$: 12.7 Hz; $^2J_{H(2)C(3)}$: 1.5 Hz.

Table 6
^{1}H NMR chemical shifts (ppm) for *trans*-cinnamic acids in $CDCl_3$ solution[a]

trans-CA	*trans*-CA-2-^{13}C	*trans*-CA-3-^{13}C	Assignment
7.571–7.547 m	7.569–7.545 m	7.577–7.541 m	H(5)
7.417–7.402 m	7.416–7.400 m	7.417–7.402 m	H(6), H(7)
7.806 d[b]	7.804 q[c]	7.803 q[e]	H(3)
6.464 d[b]	6.461 q[d]	6.463 q[f]	H(2)

[a] See footnotes a and b in Table 5.
[b] $^3J_{H(2)H(3)}$: 16.1 Hz.
[c] $^3J_{H(2)H(3)}$: 16.1 Hz; $^2J_{H(3)C(2)}$: 2.9 Hz.
[d] $^3J_{H(2)H(3)}$: 16.1 Hz; $^1J_{H(2)C(2)}$: 163 Hz.
[e] $^3J_{H(2)H(3)}$: 16.1 Hz; $^1J_{H(3)C(3)}$: 156.5 Hz.
[f] $^3J_{H(2)H(3)}$: 16.1 Hz; $^2J_{H(2)C(3)}$: 1.0 Hz.

than the coupling constants $^2J_{CC}$ for some mono-substituted benzenes where a carbon substituent is directly bonded to the ring [21]; in the case of sp^2 substituents, the former is in the range of 4.1–5.5 Hz and the latter in the range of 2.2–3.5 Hz. The trans compound shows the corresponding doublet at 128.98 ppm with a coupling constant 5.5 Hz. No splitting is observed except for 128.10 and 128.98 ppm peaks in the 130–125 ppm region for both the compounds. Therefore, the observed coupling is probably $^3J_{C(3)C(6)}$, and these peaks are assigned to the C(6). A peak at 129.97 ppm in the cis compound is ascribable to the C(5), because this signal is a doublet with a $^3J_{C(2)C(5)}$ constant 3.7 Hz in the 2-^{13}C compound. The C(5) signal of the trans compound is assigned in the same manner, but the C(5) and C(6) signals in the reverse order. These results confirm the assignment proposed by Chaloner [20].

The marked difference in the coupling constants between the cis and trans compounds is found for $^3J_{C(1)H(3)}$ in the spectra recorded in an NOE mode (gated decoupling); the value for the former is larger than that for the latter as reported for acrylic acids [22–26].

The ^{1}H NMR signals are easily assigned as in Tables 5 and 6. These assignments were confirmed by the spectra of the ^{13}C-labelled cinnamic acids. The $^2J_{H(3)C(2)}$ coupling is observed in the spectrum of *trans*-CA-2-^{13}C, but not in that of the cis compound. The $^3J_{H(2)H(3)}$ couplings of the trans acids are larger than those of the cis acids.

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Erratum

Erratum to "A comparative vibrational and NMR study of *cis*-cinnamic acid polymorphs and *trans*-cinnamic acid" [Spectrochimica Acta Part A 57 (2001) 513–519]☆

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The Publisher and Author regret that in the above article, Table 3 (page 517) was published incorrectly. It is now reproduced correctly on page 1694.

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Table 3
^{13}C NMR chemical shifts (ppm) for *cis*-cinnamic acids[a]

cis-CA[b]			*cis*-CA-2-^{13}C[c]	*cis*-CA-3-^{13}C[c]	Assignment
Solid		$CDCl_3$ soln.	$CDCl_3$ soln.	$CDCl_3$ soln.	
58°-acid	68°-acid				
172.8	172.9	171.41[d]	171.46 d[e]	171.46	C(1)(COOH)
150.8	150.4	145.89	145.88 d[f]	**145.89**	C(3)
	149.6				
134.2	136.7	134.38	134.38	134.36 d[h]	C(4)
	135.2				
131.1	129.9	129.97	129.97 d[g]	129.98	C(5)
129.6	128.8	129.4	129.4	129.4	C (7)
		128.1	128.1	128.10 d[i]	C (6)
117.6	120.5	118.68	**118.69**	118.66 d[f]	C(2)
	117.9				

[a] d, doublet.
[b] In the previous studies [9, 10].
[c] Boldface indicates the main peaks with satellites. The other signals are observed in the expanded spectra.
[d] $^3J_{C(1)H(3)}$: 14 Hz (a doublet in the spectra recorded by a gated decoupling mode).
[e] $^1J_{C(1)C(2)}$: 72.5 Hz.
[f] $^1J_{C(2)C(3)}$: 71 Hz.
[g] $^3J_{C(2)C(5)}$: 3.7 Hz.
[h] $^1J_{C(3)C(4)}$: 55 Hz.
[i] $^3J_{C(3)C(6)}$: 3.7 Hz.