Isomerism and Polymorphism of Cinnamic Acids and Deuterated Allocinnamic Acids

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Since the three polymorphic forms of allocinnamic acid were found and studied by Liebermann[1], by Paal[2], and by Biilmann[3], they have been the subject of many researches[4] including those on the dipole moment[5], the infrared absorption[6], other physical properties, and the transition between them[7].

In the course of the studies of the polymorphic behaviors of the compounds with group $C_6H_5CH=CHCO$[8], deuterated allocinnamic acids have been investigated in comparison with the ordinary allocinnamic acid, the powder X-ray diffraction and ultraviolet absorption spectra of α,β-d_2-allocinnamic acid and *O*-*d*-allocinnamic acid being measured. The X-ray diffraction patterns of the *O*-*d*-allocinnamic acid showed an expansion of the crystal lattice. No remarkable difference was found among the ultraviolet absorptions of three polymorphic forms of allocinnamic acid. In an experiment of catalytic hydrogenation of phenylpropiolic acid to allocinnamic acid, a new polymorphic form, m. p. 120°C, of (*trans*-)cinnamic acid was obtained by chance, and its transition to the stable form, m. p. 133°C, was observed.

Experimental

Partial Hydrogenation of Phenylpropiolic Acid.—Phenylpropiolic acid was prepared from commercial cinnamic acid according to the method of "Organic Syntheses"[9,10], and catalytically hydrogenated to allocinnamic acid. Palladium catalysts, e. g., Pd-$BaSO_4$[11] Pd-poly(vinyl alcohol)[12] and Pd-Na protalbinate[13], and the Urushibara catalysts[14,15], e. g., U-Ni-B and U-Co-A, were used in the partial hydrogenation and the latter catalysts were found useful for the purpose. The U-Ni-B catalyst gave the purest allocinnamic acid, while the palladium catalysts yielded hardly crystallizable products which had to be purified through the aniline salt[16]. The results of the catalytic hydrogenation with various catalysts are summarized in Table I.

The 58°-form[17] of allocinnamic acid was prepared by recrystallization of the hydrogenation products, the 68°-form through the aniline salt and the 42°-form by cooling suddenly the melt of the 58°-form or 68°-form in dry ice.

Preparation of Deuterated Allocinnamic Acids.—α,β-d_2-Allocinnamic acid was prepared by the catalytic deuteration of sodium phenylpropiolate with deuterium in a solution in 99.7% heavy water produced by the Norsk Hydro-Elektrisk Kvaelstofaktieselskab, Norway. The deuterium was generated by the electrolysis of the heavy water by using anhydrous sodium sulfate as the electrolyte, platinum electrodes, and an electric current of density 0.02∼0.03 amp./cm^2 and 6∼8 V. Palladium on barium sulfate, which was chosen on account of its small content of exchangeable hydrogen, was first deuterated in the heavy water and then employed for the catalytic deuteration. It was presumed without any determination that the α,β-d_2-allocinnamic acid contained nearly 100% deuterium in the α and β positions.

In order to deuterate the carboxylic hydrogen, allocinnamic acid was recrystallized once from 47.4% D_2O and then from 99.7% D_2O. The deuterium content of allocinnamic acid deuterated in this way was determined to be 80±5% of the carboxylic hydrogen.

Measurements of Absorption Spectra.—Ultraviolet absorptions were measured in ethanolic solution in the range of wavelengths 2100∼4000 Å with a Beckman Model DU spectrophotometer. Infrared absorptions were measured with a Baird Model B infrared recording spectrophotometer in

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[1] C. Liebermann, *Ber.*, **23**, 515 (1890); **25**, 91 (1892).

[2] C. Paal and W. Hartmann, ibid., **42**, 3931 (1909).

[3] E. Biilmann, ibid., **43**, 573 (1910).

[4] Cf. C. Weygand and H. Baumgärtel, ibid., **65**, 693 (1932); A. W. K. De Jong, *Rec. Trav. Chim. Pays-Bas*, **51**, 397 (1932).

[5] F. Eisenlohr and W. Hass, *Z. physik. Chem.*, **A173**, 249 (1935).

[6] J. Guy, *Ann. Phys.*, (12), **4**, 704 (1949).

[7] F. Eisenlohr and A. Metzner, *Z. physik. Chem.*, A, **178**, 339 (1937).

[8] F. Iimura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 1851 (1956).

[9] T. W. Abbott, "Organic Syntheses", Col. Vol. 2, John Wiley & Sons, New York (1948), p. 515.

[10] T. W. Abbott and D. Althousen, ibid., Col. Vol. 2, (1948), p. 270.

[11] R. Mozingo, ibid., Vol. 26, (1946), p. 77.

[12] L. D. Rampino and F. F. Nord, *J. Am. Chem. Soc.*, **63**, 2745 (1941).

[13] C. Paal and C. Amberger, *Ber.*, **38**, 1398 (1905).

[14] Y. Urushibara and S. Nishimura, This Bulletin, **27**, 480 (1954).

[15] Y. Urushibara, S. Nishimura and H. Uehara, ibid., **28**, 446 (1955).

[16] C. Liebermann, *Ber.*, **27**, 2037 (1894).

[17] "58°-Form" denotes the polymorphic form melting at 58°C and so on.

TABLE I. PARTIAL HYDROGENATION OF PHENYLPROPIOLIC ACID WITH VARIOUS CATALYSTS*

Catalyst	Conditions of hydrogenation	Forms of cinnamic acid obtained
U-Ni-B	Na salt in water	*cis*-58°**
U-Ni-A	Acid in ethanol	*cis*-58°
U-Co-A	Na salt in water	*cis*-58°, *cis*-68°
U-Co-A, then U-Ni-A	Acid in ethanol	*trans*-120°
U-Co-B	Na salt in water	*cis*-58°**
Pd-Na protalbinate (colloidal)	Na salt in water	Oil, *cis*-68° through aniline salt
Pd-charcoal	Na salt in water	Oil, *cis*-68° by recrystallization
Pd-$BaSO_4$	Na salt in water	*cis*-58°
Pd-poly(vinyl alcohol) (colloidal)	Na salt in water	Oil (*cis*-58°)**
U-Ni-B and active charcoal	Na salt in water	*cis*-68°, *cis*-58°

* Hydrogenation was stopped when one mole of hydrogen was absorbed.

** Phenylpropionic acid was obtained.

Nujol and in carbon tetrachloride solution when necessary.

Measurements of X-ray Diffraction Patterns. — The powder method was used with a Norelco X-ray diffractometer. The identity and the difference among polymorphic forms were determined by the diffraction patterns, the diffraction angles being mainly taken into consideration for the identification and the intensity of the diffracted beams being only auxiliarily respected.

Results and Discussion

Ultraviolet Absorption.—Guy[18] observed that polymorphic forms of allocinnamic acid give different infrared spectra especially in the finger print region, and Urushibara, Iimura and Ikeda[8,19] showed that polymorphic forms of chalcones differ not only in infrared but also in ultraviolet spectra. The ultraviolet absorptions of cinnamic acid and allocinnamic acid have been reported with no notice of any difference in polymorphic forms[20].

TABLE II. ULTRAVIOLET ABSORPTION SPECTRA OF CINNAMIC ACIDS IN ETHANOL

	Form	λ_{max}(Å)	ε_{max}
Cinnamic acid	133°	2730	20500
(*trans*)	120°	2725	19000
Allocinnamic acid	58°	2670	9500
(*cis*)	68°	2660	9800
	42°	2630～2650	ca.10000

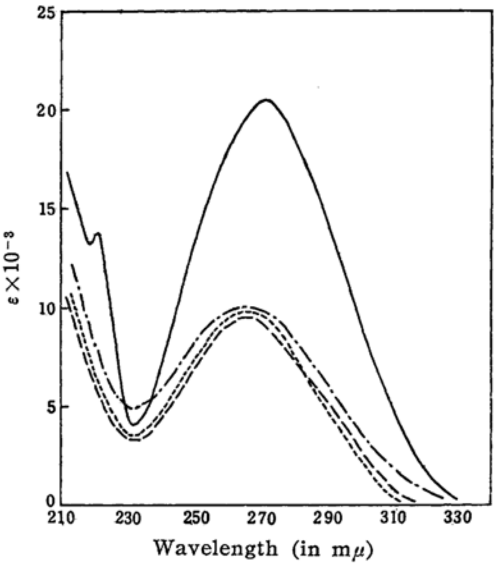

Fig. 1. The ultraviolet spectra of cinnamic acids.
Cinnamic acid 133°-form ———
Allocinnamic acid 42°-form —·—·—
58°-form ···········
68°-form - - - - -

Ultraviolet absorption spectra in ethanol were measured with all the polymorphic forms of cinnamic acid and of allocinnamic acid with the results shown in Table II and Fig. 1. The three forms of allocinnamic acid gave similar absorption curves with no remarkable differences in either the locations or the intensities of the absorption maxima. Moreover, cinnamic acid and allocinnamic acid absorbed almost the same wavelength but the intensity of the former was roughly twice as strong as the latter.

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[18] J. Guy, *Ann. Phys.*, (12), **4**, 704 (1949).

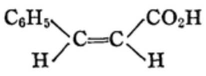
[19] Y. Urushibara, F. Iimura and K. Ikeda, *J. Chem. Phys.*, **22**, 1943 (1954); **23**, 759 (1955); F. Iimura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 1846 (1956).

[20] A. E. Gilam and E. S. Stern, "Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", Edward Arnold Ltd., London (1954); H. M. Hershenson, "Ultraviolet and Visible Absorption Spectra, Academic Press Inc., New York (1956), p. 233.

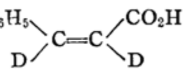
Braude and his co-workers[21-23] have extensively studied the relations between the ultraviolet spectra and the steric hindrance in conjugated systems and concluded that, when the steric hindrance is not so large as to prevent the conjugation, the sterically hindered *cis*-isomer gives an absorption maximum almost at the same location as the unhindered *trans*-isomer but having a remarkably lower intensity. The appearance of polymorphism in a molecule with a partially hindered conjugated system is caused by the existence of metastable, rotationally hindered, forms conditioned by both the steric hindrance and the π-electron interaction between two parts of the molecule[24,25]. The interpretation that the polymorphism of cinnamic acids is based on such causes is supported by the different infrared spectra of the polymorphic forms.

The ultraviolet spectra of the deuterated allocinnamic acids revealed no isotope effect in any polymorphic forms.

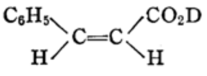
Polymorphism of Deuterated Allocinnamic Acids.—Measurements of the powder X-ray diffraction with α,β-d_2-allocinnamic acid (II) and O-d-allocinnamic acid (III) in comparison with the ordinary allocinnamic acid (I) showed that the diffraction patterns of the polymorphic forms of O-d-allocinnamic acid deviate from those of the corresponding forms of the other two, respectively. The deviations are comparatively remarkable, though small, in the two polymorphic forms melting at 58°C and at 68°C, and noticeably in the direction of smaller diffraction angles, suggesting a lattice expansion caused by deuteration. Deviations observed in the 42°-form permit to conclude neither a lattice expansion nor a lattice contraction.



(I)



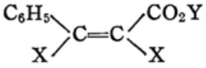
(II)



(III)

The lattice expansion observed in the two forms of O-d-allocinnamic acid is supposed to be due to the deuterium bond which is weaker than the hydrogen bond in the corresponding forms of the ordinary allocinnamic acid. Such an isotope effect is known in oxalic acid[26] and other compounds[27] and explained on the basis of the weaker deuterium bond.

TABLE III. THE MELTING POINTS OF ALLOCINNAMIC ACIDS



Form	I	II	III
	X=Y=H	X=D, Y=H	X=H, Y=D
68°	67.5～68.0°	67.0～68.0°	66.5～67.0°
58°	57.5～58.5°	55.0～57.5°	54.5～55.0°
42°	41.0～42.5°		41.5～42.0°

Some forms of the deuterated allocinnamic acids melted lower than the corresponding forms of the ordinary allocinnamic acid, as shown in Table III, and, since the melting point of either the 58°-form or the 68°-form of the ordinary allocinnamic acid was lowered by recrystallization from heavy water, it can be concluded that the lowering of the melting points of O-d-allocinnamic acid is connected with the lattice expansion.

Formation and Properties of the Metastable Form, m. p. 120°C, of Cinnamic Acid.—The new form of (*trans*-)cinnamic acid was obtained in an experiment to prepare allocinnamic acid from phenylpropiolic acid. The experimental sequence was as follows: When phenylpropiolic acid was hydrogenated with the U–Co–A catalyst, the reaction was too slow to be completed. Then U–Ni–A was added with an intension of finishing the partial hydrogenation to allocinnamic acid. After being left to stand for a day, the product was isolated from the reaction mixture, but it melted at 120°C and did not coincide with any form of allocinnamic acid. The product proved a new form of (*trans*-)cinnamic acid, since it gave an infrared absorption in solution quite similar to that of the known form (m. p. 133°C) of cinnamic acid except for a slight difference in the finger print region, and an ultraviolet absorption also similar to that of the 133°-form of cinnamic acid (120°-form: λ_{max} 2725 Å, ε_{max} 19000; 133°-form: λ_{max} 2730 Å, ε_{max} 20500). On the other hand,

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21) E. A. Braude et al., *J. Chem. Soc.*, **1949**, 1890.

22) E. A. Braude and F. Sondheimer, ibid., **1955**, 3754.

23) E. A. Braude and C. J. Timmons, ibid., **1955**, 3766.

24) B. Eistert, F. Weygand and E. Csendes, *Ber.*, **84**, 745 (1951).

25) B. Eistert, F. Weygand and E. Csendes, ibid., **85**, 164 (1952).

26) M. J. Robertson and A. R. Ubbelhde, *Proc. Roy. Soc.*, **A170**, 222 (1939).

27) Benzoic acid, succinic acid, sodium bicarbonate, etc.

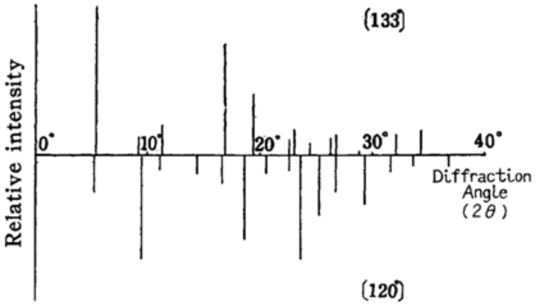

Fig. 2. The X-ray diffraction patterns of the 120°-form and the 133°-form of (*trans*-)cinnamic acid.

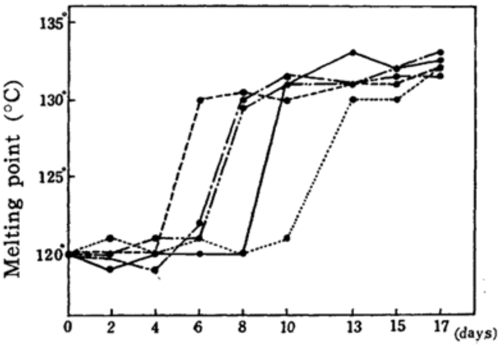

Fig. 3. Changes of the melting points of the 120°-form of cinnamic acid.

the X-ray diffraction pattern of the 120°-form is clearly different from that of the stable 133°-form of cinnamic acid, as shown in Fig. 2.

The formation of the new form of cinnamic acid in the hydrogenation of phenylpropiolic acid is explained by assuming that the allocinnamic acid formed by the catalytic hydrogenation was isomerized to a metastable form of the *trans*-isomer during its contact with the catalyst. The 120°-form was transformed into the 133°-form in one week or two, when it was kept in a dark place at room temperature. All attempts to repeat the preparation of the metastable form failed and the *cis*-isomer was always obtained instead. Further, it was observed that the transition of the metastable form to the stable form occurred abruptly when it once started by chance. Namely, when five portions of the metastable form were kept in a dark place at about 15°C, the melting points of these portions, determined every second or third day, changed suddenly but at different times, as shown in Fig. 3.

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