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Thermally Derived Dimers of *o*-Vinylphenol: *trans*- and *cis*-2′-Hydroxy-4-methylflavans

Yen-Yuan CHEN, Ryuichi OSHIMA, and Ju KUMANOTANI*
Institute of Industrial Science, The University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106

(Received August 27, 1982)

Synopsis. *o*-Vinylphenol dimerizes thermally to yield quantitatively two isomers, *trans*- and *cis*-2′-hydroxy-4-methylflavans. The analysis of the dimers of *o*-vinylphenol-*O*-*d* suggests that a quinone-methide intermediate is responsible for the formation of these flavanoid compounds.

Although a number of papers have been published concerning the radical polymerization of *o*-vinylphenol,[1–5] little is known of its dimers formed in the course of the polymerization or during storage.[1] Flavanoid compounds were previously found in our laboratory to be obtained by the dimerization of *o*-vinylphenol; they were assumed to be mixtures of *cis* and *trans* isomers.[2] In this paper, we report the identification of each isomer of the dimers separated by gel-permeation chromatography (GPC) and liquid-solid chromatography (LSC).

Experimental

Thermal Dimerization. *o*-Vinylphenol (1.0 g) (bp 61 °C/3—4 mmHg (1 mmHg = 133.322 Pa), made by the decarboxylation of *o*-coumaric acid)[6,7] was heated at 90 °C for 12 h in an ampoule displaced with nitrogen; the dimers were thus obtained almost quantitatively, along with a trace of higher-molecular-weight substances (less than 1%), which has been separated by GPC on a preparative TSK-gel 2000HG8 column (2.2 cm I.D. × 60 cm × 2), using chloroform as the eluent. The dimers were fractionated by LSC (1 : 3 in a peak-area ratio with a UV detector at 254 nm) on a semi-preparative silica column (Nomura Chemical, Develosil 60-3, 8 mm I.D. × 25 cm), using hexane–ethyl acetate (95.5: 2.5 v/v) as the eluent.

The ^{1}H NMR spectra of these two isomers were recorded at 90 MHz with a Varian EM 390 spectrometer, using tetramethylsilane as the internal standard in $CDCl_3$.

The minor isomer was obtained as a white solid; mp 86 °C; mass spectrum, *m*/*e* 240 (M^+). Found: C, 79.61; H, 6.73%. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%.

The major isomer was obtained as a pale yellow viscous liquid; mass spectrum, *m*/*e* 240 (M^+). Found: C, 79.31; H, 6.75%. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%.

Dimerization of o-*Vinylphenol*-O-d. A mixture of 1.0 g of *o*-vinylphenol, 10 ml of carbon tetrachloride, and 1 ml of deutrium oxide was shaken vigorously for 20 min, after which the separated oily layer was again shaken with new deuterium-oxide (1 ml) for 30 min. The oily layer was separated and dried over sodium sulfate. The IR spectrum of the solution confirmed the complete H–D exchange at the hydroxyl group of *o*-vinylphenol. Then the solution was transferred into an ampoule. After the removal of carbon tetrachloride *in vacuo*, the ampoule was sealed under nitrogen and heated at 90 °C for 12 h. The dimers were then separated into two isomers by means of LSC, as has been described above. Mass spectra for both isomers: *m*/*e* 241 (M^+).

Results and Discussion

Each of the fractionated isomers showed the same *m*/*e* value (240) for the molecular ion and similar IR spectra. In the IR spectra of the isomers, the absorption bands due to a vinyl group (1630, 1420, and 910 cm^{-1}) were completely eliminated, and a new band, presumably due to an ether group, appeared at 1050 cm^{-1}. The ^{1}H NMR spectra of both isomers are shown in Fig. 1. By extensive decoupling experiments, each resonance

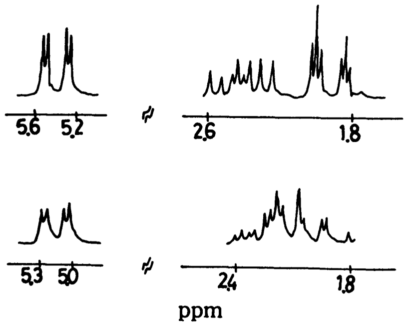
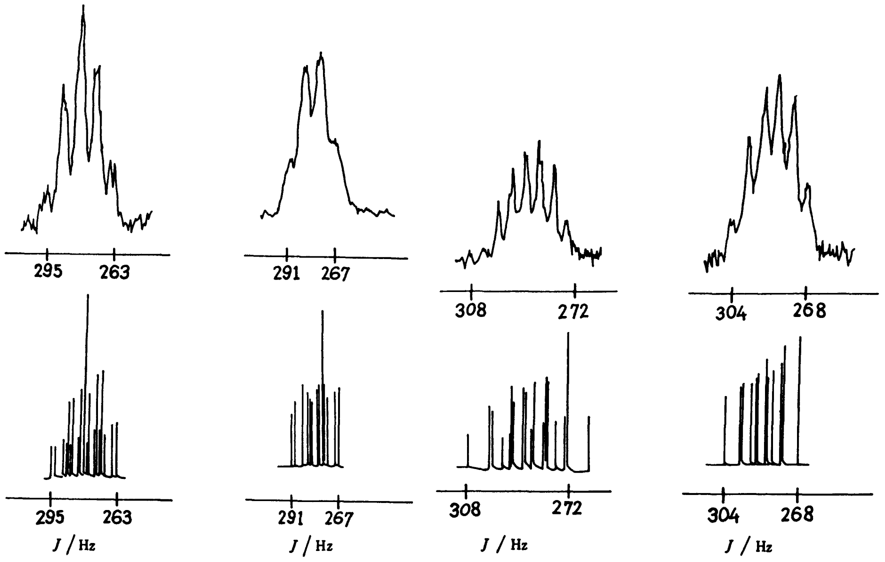


Fig. 1. ^{1}H NMR spectra of *o*-vinylphenol dimers (H_2, H_{3e}, and H_{3a}): above, *trans* and below,*cis*.



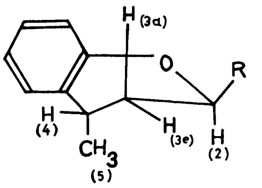
(a) (b)

Fig. 2. ^{1}H NMR spectra of H_4: (a), *trans* isomer and (b), *cis* isomer; left, undeuterated and right, deuterated; above, observed and below, calculated. The chemical shifts were expressed in Hz from TMS.

Table 1. ^{1}H NMR data of *trans*- and *cis*-2′-hydroxy-4-methylflavans

Chemical shift$^{a)}$ (δ) of	*trans*	*cis*
H_2(1H)	5.30	5.25
H_{3e}(1H)	1.95	2.28
H_{3a}(1H)	2.43	1.97
H_4(1H)	3.10	3.17
H_5(3H)	1.45	1.37
Coupling constants/Hz		
3a, 3e	14	15
3e, 4	2	7
2 , 3e	3	3
3a, 4	6	13
2 , 3a	12	12
4 , 5	8	8

a) Measured at 90 MHz in $CDCl_3$. Chemical shifts (center of multiplet) are shown in δ.



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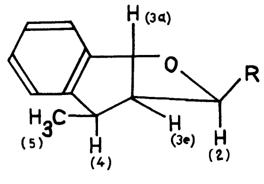
$R=-C_6H_4OH$



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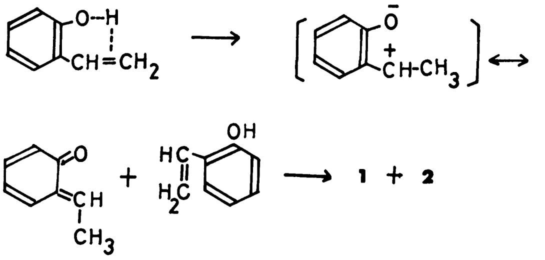
was assigned as is summarized in Table 1 : in the minor product, $J_{3e,4}$ (2 Hz) corresponds to $J_{eq,eq}$, and $J_{3a,4}$ (6 Hz) to $J_{ax,eq}$, while in the major product, $J_{3e,4}$ (7 Hz) and $J_{3a,4}$ (13 Hz) stand for $J_{eq,ax}$ and $J_{ax,ax}$ respectively. From these results, it is obvious that the minor isomer has the 2,4-*trans* structure (**1**) with a quasi-axial methyl group, while the major isomer has the 2,4-*cis* structure (**2**) with a quasi-equatorial methyl group at C-4 of the flavanoid compounds. The coupling constants also indicate that the *o*-C_6H_4OH group is in the quasi-equatorial position for both isomers.[8] Accordingly, it may be concluded that the minor and major isomers are *trans*- and *cis*-2′-hydroxy-4-methylflavans, respectively.

The predominant formation of the *cis* isomer may be explained on steric effect: the *cis* isomer has both substituents at quasi-equatorial positions with less crowding than in the *trans* isomer, which has the quasi-axially oriented methyl group.

The dimers from *o*-vinylphenol-*O*-*d* showed a weak C–D absorption band at 2230 cm^{-1} and an m/e value of 241 for M^+. In the ^{1}H NMR spectra, no significant difference could be detected for the peaks due to H_2, H_{3a}, and H_{3e}. However, peaks from H_4 and H_5 of both isomers were obviously different from those of undeuterated dimers. The integrated intensity of the resonance of H_5 for both isomers decreased to 2/3 of that for undeuterated isomers, and the peak became a doublet of triplets with a new, small coupling (J=1.2 Hz) which can be attributed to a geminal deuterium-proton coupling.[9] The splitting of the H_4 peak is also consistent with the calculated ones.[10] (see Fig. 2)



Scheme 1. A mechanism of thermal dimerization of *o*-vinylphenol.

Consequently, Scheme 1 can be taken as a mechanism of the dimerization of *o*-vinylphenol. It may be suggested that the initial migration of the proton of the phenolic hydroxyl group, making a hydrogen-bond bridge with the neighbouring vinyl group, leads to the formation of quinone methide[11] through a dipolar intermediate. Then it may react with an olefin (*o*-vinylphenol) to give the dimers by means of a Diels-Alder reaction.[12,13] This mechanism may also account for the formation of a similar type of flavanoid compound obtained from 4-isopropenyl-*m*-cresol.[14–16] When compared with styrene, which thermally gives *cis*- and *trans*-1,2-diphenylcyclobutanes as the dimers,[17] the phenolic hydroxyl group may play a significant role in the thermal dimerization of *o*-vinylphenol.

References

1) T. Tanaka, T. Yamashita, and T. Yokoyama, *Kogyo Kagaku Zasshi*, **60**, 1595 (1957).

2) J. Kumanotani and K. Oshima, paper presented at a meeting of the Society of Polymer Science, Japan, June 5th, 1964.

3) M. Kato and H. Kamogawa, *J. Polym. Sci., Part A-1*, **4**, 2771 (1966).

4) M. Kato and H. Kamogawa, *J. Polym. Sci., Part A-1*, **4**, 2771 (1966).

5) K. Hiraoka and T. Yokoyama, *Reports of the Faculty of Engineering*, Nagasaki University, **7**, 95 (1976).

6) W. J. Dale and H. E. Hennis, *J. Am. Chem. Soc.*, **80**, 3645 (1958).

7) B. B. Corson, W. J. Heintzelman, L. H. Schwartzman, H. E. Tiefenthal, R. J. Lokken, J. E. Nickels, G. R. Atwood, and F. J. Pavlik, *J. Org. Chem.*, **23**, 544 (1958).

8) B. J. Bolger, A. Hirwe, K. G. Marathe, E. M. Philbin, and M. A. Vikars, *Tetrahedron*, **22**, 621 (1966).

9) R. M. Silverstein, G. C. Bassler, and T. C. Morrill, "Spectrometric Identification of Organic Compounds," 4th ed, John Wiley and Sons, New York (1981), p. 199.

10) Spectra were calculated by means of the JEOL simulation program (JEOL, Ltd., Tokyo, Japan), using the data in Table 1.

11) A. Turner, *Quart. Rev.*, **18**, 347 (1964).

12) G. R. Sprengling, *J. Am. Chem. Soc.*, **74**, 2927 (1952).

13) K. Hultzsch, *Ber.*, **74**, 898 (1941).

14) W. Baker and D. H. Bestly, *Nature*, **144**, 865 (1939).

15) W. Baker and D. H. Bestly, *J. Chem. Soc.*, **1940**, 1103.

16) W. Baker, R. F. Curtis, and J. F. Mcomie, *J. Chem. Soc.*, **1951**, 76.

17) V. K. Kirchner and K. Bucholz, *Angew. Makromol. Chem.*, **13**, 127 (1970).