A New Type of Phenylpropane from the Essential Fruit Oil of *Pimpinella anisum L.*

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From the essential oil of *Pimpinella anisum* fruits a hitherto unknown type of phenylpropane was isolated. The mass, infrared, and ^{13}C NMR spectra indicate, that the unknown is a 2-methyl-butyric acid ester of 2-hydroxy-5-methoxy-*trans*-propenylbenzene.

Biosynthetic pathways to derivatives of phenylpropane containing oxygen bonded substituents normally result in the introduction of one substituent at C-4. In this respect we wish to report the isolation of a hitherto unknown type of phenylpropane from the essential oil of the fruit of Pimpinella anisum L. The mass spectrum ($M^+ = m/e$ 248; base peak = m/e 104), the infrared spectrum and analysis by gas chromatography indicate, that the unknown is a (methoxy, *trans*-propenyl)-phenol ester of 2-methyl-butyric acid. A normal structure would be based on the appropriate ester of *trans*-isoeugenol, but this was dismissed by virtue of G. C. retention times. We turned our attention therefore to the possibility of an alternative arrangement of the three ring substituents. From the ^1H NMR spectrum the olefin side chain ($\delta = 1.87$, 6.10, 6.29), the methoxy group ($\delta = 3.76$), the 2-methyl-butyric acid fragment ($\delta = 1.0$, 1.07, 1.28, 2.57) and the three aromatic protons ($\delta = 6.8$ (2 H) and 6.98 (1 H)), are evident. The relative positions of the three substituents however, were not forthcoming from this data.

The ^1H-broad band decoupled ^{13}C NMR spectra[1] of the aromatic carbons of the unknown, of *trans*-isoeugenol and of the *trans*-isoeugenol ester of 3-methyl butyric acid, together with the calculated[2] position of each line are summarized in Table I. As is shown the chemical shifts of all ring carbons, in particular thoseof *trans*-isoeugenol-3′-methylbutyric acid ester, can be accurately predicted. Based on previous data, a symmetrical or vicinal arrangement of the substituents in the unknown would be unlikely. Chemical shift data for the ring C-atoms of the five remaining possible structures were therefore calculated (using groups as closely analogous as possible to those in the unknown) and compared to those found (Table II).

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Table I. Comparison of ^{13}C NMR chemical shift data for isoeugenol (**1**) and its 3-methyl-butyric acid ester (**2**) with calculate[2,3] (**1a**, **2a**) and previously reported[4] (**1b**) values.

	Substituents						Chemical shift[a,b]					
	C-1	C-2	C-3	C-4	C-5	C-6	C-1	C-2	C-3	C-4	C-5	C-6
1	–CH=CH–CH$_3$	—	–OCH$_3$	–OH	—	—	131.9	*111.5*	146.8	144.1	*114.7*	*121.3*
1a	–CH=CH–CH$_3$	—	–OCH$_3$	–OH	—	—	131.9	*113.4*	147.1	140.1	*116.9*	*120.0*
1b	–CH=CH–CH$_3$	—	–OCH$_3$	-OH	—	—	131.0	*109.9*	148.5	146.5	*115.8*	*119.9*
2	–CH=CH–CH$_3$	—	–OCH$_3$	–OR[c]	—	—	137.5	*108.9*	151.2	138.5	*123.0*	*118.1*
2a	–CH=CH–CH$_3$	—	–OCH$_3$	–OAc	—	—	137.5	*112.9*	153.3	136.2	*123.1*	*119.5*

[a] Shifts were measured in ppm downfield of internal TMS in $CDCl_3$ solution.
[b] Chemical shifts for the unsubstituted carbons are italic.
[c] R = –CO–CH$_2$–CH=(CH$_3$)$_2$.

Table II. Comparison of ^{13}C NMR chemical shift data of the unknown component from ethereal fruit oils of *Pimpinella anisum* L. (**4**) with calculated values (**3a**–**3e**).

	Substituents						Chemical shift[a,b]					
	C-1	C-2	C-3	C-4	C-5	C-6	C-1	C-2	C-3	C-4	C-5	C-6
3a	–CH=CH–CH$_3$	—	–OAc	–OCH$_3$	—	—	132.2	*120.7*	137.0	152.5	*115.3*	*124.8*
3b	–CH=CH–CH$_3$	–OCH$_3$	—	–OAc	—	—	122.0	158.6	*107.6*	151.7	*114.2*	*128.4*
3c	–CH=CH–CH$_3$	–OAc	—	–OCH$_3$	—	—	124.5	150.1	*107.6*	160.2	*111.7*	*128.4*
3d	–CH=CH–CH$_3$	–OCH$_3$	—	—	–OAc	—	135.4	155.0	*115.3*	*122.3*	142.6	*120.7*
3e	–CH=CH–CH$_3$	–OAc	—	—	–OCH$_3$	—	133.4	141.2	*123.1*	*114.5*	157.4	*112.3*
4	–CH=CH–CH$_3$	–OR[c]	—	—	–OCH$_3$	—	131.4	141.6	*123.3*	*113.3*	157.3	*111.1*

[a,b] Same as in Table I; [c] R = –CO–CH(CH$_3$)–CH$_2$–CH$_3$.

An arrangement of the substituents based on that in compound **3e** is clearly indicated. The splitting in the ^{1}H off-resonance decoupled spectrum also supports this structure, as does the gated decoupled spectrum.

In the latter an intense sharp doublet is found for the C-3 carbon. A similar signal is also observed for the C-5 in *trans*-isoeugenol-3′-methyl-butyric acid ester, and the origin of the characteristic phenomenon will be discussed in a later publication.

The positions of the signals of the substituents in the unknown occur according to expectations. The unknown is therefore the 2-methyl-butyric acid ester of 2-hydroxy-5-methoxy-*trans*-propenyl-benzene. Our complete NMR assignments are summarized in Fig. 1.

To our knowledge this is the first report of a divergence from the normal configuration of the oxygen-bonded substituents in this type of compound. Our results therefore reflect unfavourably on those theories, which predict a biosynthetic pathway leading to an isoeugenol like structure for phenylpropanes of this type.

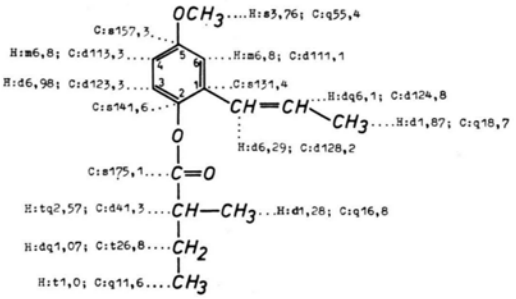

Fig. 1. Complete NMR assignments for the unknown component from the essential oil of the fruit of *Pimpinella anisum L.*

^{1}H and ^{13}C data are denoted by 'H' and 'C', respectively. The splittings in the ^{13}C data refer to the off-resonance spectra. Chemical shifts were all measured in $CDCl_3$ solution and are expressed in δ-values relative to internal TMS.

[1] Spectra were measured at 22.63 MHz on a WH-90 spectrometer.

[2] J. B. Stothers, Carbon-13 NMR Spectroscopy, p. 197, Academic Press, New York and London 1972.

[3] Substituents effect data for $-CH=CH-CH_3$ were taken from an anisol spectrum in $CDCl_3$; C-1 = +11.1, o = −1.6, m = +0.8, p = 0.0.

[4] H.-D. Lüdemann and H. Nimz, Macromol. Chem. **175**, 2393 [1974].