Phenylpropanoic Acid Esters in the Essential Oil of *Cistus ladanifer* L. (Cistaceae)

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Essential Oils, *Cistaceae, Cistus ladanifer,* Phenylpropanoic acid esters, NMR- and MS-Data

Esters of phenylpropanoic acid with 2-phenyl-ethanol-1 and the homologue, 3-phenyl-propanol-1 as well as geraniol and dehydrogeraniol were found in the essential oil of *Cistus ladanifer.* The isolation of these esters by chromatographic methods and structural elucidation by NMR and MS are described.

Introduction

Some species of the mediterranean genus *Cistus* secrete large amounts of essential oils from their leaves [1 – 3]. These *Cistus* oils are often used for perfumery [4], especially the very complex essential oil of *Cistus ladanifer,* consisting of several hundred compounds [5 – 7].

In this paper the occurrence of phenylpropanoic acid esters in the essential oil of *Cistus ladanifer* is reported. The unesterified phenylpropanoic acid has already been isolated from essential oils and plant aroma extracts [8 – 16], including the essential oil of *Cistus ladanifer* [7, 17]. Until now, however, only one ester of phenylpropanoic acid, 2-phenylethanol-1-phenylpropanoate, was identified in plant aromas, in the "absolues" of the male flowers of *Alnus sieboldiana* [9]. Esters of phenylpropanoic acid with monoterpene alcohols, as reported in this paper, have thus far not been described.

Materials and Methods

The *Cistus* plants were grown from seeds and cultivated in the field of the Botanical Institute of the University of Köln. Extraction of essential oils was carried out by steamdestillation. Fractionation of the oil according to functional groups was achieved by SiO_2-column chromatography [5, 6]. Esters and carbonyl compounds were eluted with 2-chloropropane. This fraction was further separated into four fractions by preparative TLC (TLC-plate 40 × 20 cm, SiO_2 60 GF_{254} from Merck, Darmstadt, layer 0,5 mm), solvent system petrol ether/1,2 dichlorethane (2 : 1 v/v). Fractions with Rf-values 0.15 and 0.27 included phenylpropanoic acid esters.

Further purification was achieved by repeated TLC on SiO_2 plates (TLC-plate 20 × 20 cm, SiO_2 60 G, Merck, Darmstadt, layer 0.25 mm) which were impregnated with 1 g $AgNO_3$ being dissolved in 10 ml acetonitrile, solvent system 1,2 dichloroethane. Spray reagents were dichlorofluorescein or bromothymol blue. If necessary further purification was achieved by TLC (SiO_2 GF_{254}, Merck, Darmstadt) solvent system *n*-pertane/ether (95 : 5 v/v).

The esters were hydrolysed with 0.5 n KOH for one hour under refluxing, the free phenylpropanoic acid was methylated with diazomethane. Reduction of the esters was carried out in dry ether with $LiAlH_4$.

GC: Hewlett-Packard, model 583O A with 1885O A GC-Terminal; glascapillary-Columns:

stat. phase	temperature
10 m Sp 2100	50 ° – 170 °C, 30′ isotherm
25 m FFAP	50 ° – 220 °C, 50′ isotherm
25 m OV 101	50 ° – 250 °C, 10′ isotherm

IR: Perkin-Elmer, model Infracord 137, film between KBr-pellets.

NMR: 60 MHz: Hitachi Perkin-Elmer, model R-24 B. 90 MHz: Varian, model EM 390.

GC-MS: Finnigan, model 3200, electron energy 70 eV (EI) or 120 eV (CI).

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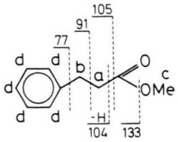
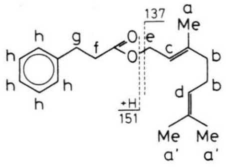
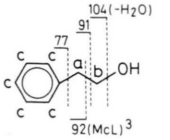
Table I. Structure and Spectral Data from Isolated Phenylpropanoic Acid Esters and their Saponification Alcohols



I



II



III

NMR[1]				MS (EI)		NMR				MS (CI)[2]		NMR				MS (EI)	
H	δ	*J*	*I*	*m/e*	int[4]%	H	δ	*J*	*I*	*m/e*	int %	H	δ	*J*	*I*	*m/e*	int %
a	t 2.6	6	2	164 M⁺	10	a	s 1.6	–	3	287	17	a	t 2.7	6	2	122 M⁺	30
b	t 2.7	6	2	133	5	a′	s 1.7	–	6	286 M⁺	15	b	t 3.7	6	2	104	5
c	s 3.5	–	3	105	35	b	t 2.0	2	4	151	10	c	s 7.0	–	5	92	90
d	s 6.9	–	5	104	100	f	t 2.6	6	2	137	100					91	100
				91	80	g	t 2.7	6	2	136	20					77	10
				77	30	c	d 4.2	8	1								
						d	t 5.0	2	1								
						e	t 5.5	8	2								
						h	s 6.9	–	5								

[1] NMR-spectra **I–III** are recorded at 60 MHz, spectra **V** and **VI** at 90 MHz ($CDCl_3$ or CCl_4, TMS), δ-values in ppm, *J*-values in Hz, *I* number of protons.
[2] CI–(i–C_4H_{10}).
[3] McLafferty rearrangement.
[4] Relative intensity in %.

Results and Discussion

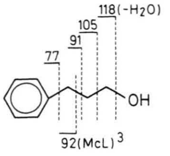
Four thus far not identified compounds could be isolated by chromatographic methods from the essential oil of *Cistus ladanifer*. The IR-spectra indicate that these four compounds are aryl esters (1750 cm^{-1}, strong: ester; 1500 cm^{-1}, medium: aromatic ring; 750 and 700 cm^{-1}, strong: monosubstituted benzene ring). Saponification yielded the same acid in each case. The four compounds differed therefore only in their alcoholic component. Reduction of the esters confirmed these results. The identification of the acid (as methyl ester **I**) and of the alcohols (**III–VI**) after saponification was achieved by NMR- and mass spectrometry. The fragmentation pattern of **I** agrees well with data given in the literature for 3-phenylpropanoic acid methyl ester [16, 18, 19] and the NMR-spectrum is identical with that of an authentic sample obtained from cinnamic acid (Table I).

2-Phenyl-ethanol-1 (**III**) and 3-phenyl-propanol-1 (**IV**) were identified from their spectral data [20, 21], (Table I). From geraniol (**V**) a CI (i–C_4H_{10}) spectrum could be obtained. Since the *cis/trans*-isomers geraniol and nerol cannot be distinguished by their EI-spectra [22] identification was achieved NMR-spectroscopically by comparison with authentic material and by GLC analysis.

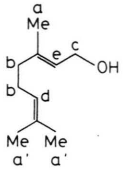
From the CI (i–C_4H_{10}) spectrum of **VI** it was concluded that this compound differed from geraniol by the presence of an additional double bond. The structure of **VI** follows from the NMR spectrum (Table I): The signals at 1.7 and 1.8 ppm correspond to two vinylic methyl groups (a and a′). Analogous shifts are observed in the spectrum of geraniol. A singlet at 4.9 ppm stems from a terminal methylene group ($C=CH_2$). Signals at 4.2 and 5.5 ppm (coupling with each other as shown by double resonance experiments) correspond – as in the spectrum of geraniol – to c and e. The methylene doublet at 2.8 ppm (b) collapses to a singlet upon irradiation at 5.7 ppm (olefine proton). Coupling to no other proton could be detected. Irradiation at 2.8 ppm in turn reduces the multiplicity of f (double triplet) to a doublet ($J = 16$ Hz). The same *J* is observed with the signal of g (6.2 ppm). The size of the coupling constant is in agreement with E-substitution of the double bond.

Thus far the NMR data would be in agreement with the isomeric structure **VII** as well. Double resonance experiments allow a distinction in favor of **VI**:

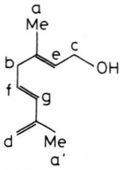
Continued (Tab. I).



IV



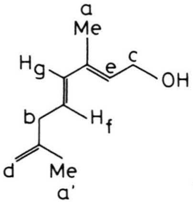
V



VI

IV NMR	IV MS (EI)		V NMR				V MS (CI)		VI NMR				VI MS (CI)	
	m/e	int %	H	δ	*J*	*I*	*m/e*	int %	H	δ	*J*	*I*	*m/e*	int %
	136 M^+	10	a	s 1.6	–	3	155	5	a	s 1.7	–	3	153	30
	118	40	a'	s 1.7	–	6	154 M^+	20	a'	s 1.8	–	3	152 M^+	20
	117	65	b	s 2.0	–	4	137	90	b	d 2.8	8	2	135	100
	105	15	c	d 4.2	8	2	136	5	c	d 4.2	8	2	134	5
	103	13	d	t 5.0	–	1	81	100	d	s 4.9	–	2	107	25
	92	50	e	t 5.5	8	1	69	10	e	t 5.5	8	1	93	40
	91	100							f	dt 5.7	16	1		
	77	15							g	d 6.2	16	1		

Irradiation at 2.8 ppm (b) not only results in a simplification of the coupling pattern of f, but also in a sharpening of the signal of g broadened by allylic coupling of the latter with b. In the case of structure **VII** one would observe, instead a broadening of the signal of the terminal CH_2-group d (4.9 ppm) which should disappear upon irradiation at 2.8 ppm. Since neither effect has been observed structure **VII** can be excluded.



VII

Geranyl-phenylpropanoate **II** will be an example for the spectroscopic identification of one of the native phenylpropanoic acid esters in the essential oil of *Cistus ladanifer*. The interpretation of the spectral data (Table I) agrees with that for **I** and **V**.

Other compounds of the 2-chloropropane fraction will be published soon.

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