Phytochemistry, Vol. 20, No. 4, pp. 828–830, 1981.
Printed in Great Britain.

0031-9422/81/040828-03 $02.00/0

TERPENOIDS OF THE ESSENTIAL OIL FROM *MOLOPOSPERMUM PELOPONNESIACUM* ROOTS*

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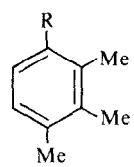
(*Received* 19 *July* 1980)

Key Word Index—*Molopospermum peloponnesiacum*; Apiaceae; essential oil constituents; gas chromatography; spectroscopy.

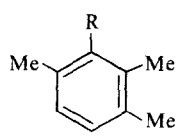
Abstract—The investigation of the essential oil from *Molopospermum peloponnesiacum* roots afforded, in addition to some well known terpenoids, two aromatic aldehydes, which were found for the first time as volatile oil components. Their structures were elucidated by spectroscopic methods. The formation of these aldehydes during steam distillation from unstable precursors is discussed.

INTRODUCTION

Molopospermum peloponnesiacum (L.) Koch is an orophilic perennial plant from the montane and subalpine zones of the southern Alps and the Pyrenees. The systematic position of this monotypic genus within the subfamily Apioideae is not clearly defined on the basis of morphology [1]. The few phytochemical characters reported [2, 3] do not allow chemosystematic conclusions to be drawn. However, *M. peloponnesiacum* contains a large amount of volatiles, and the distinctive odour of the plant suggests there must be some specific components present. This paper deals with the isolation and elucidation of the main components of the essential oil of the root.



14 R = CHO
15 R = COOH



16 R = CHO
17 R = COOH

RESULTS

The essential oil, obtained by steam distillation of fresh roots, was analysed by capillary GLC and by coupled GC–MS. Thirteen well known terpenoids (**1**–**13**) were detected for the first time in *M. peloponnesiacum* (Table 1). The main component was the monoterpene hydrocarbon 3-carene with about 45% of the total oil. In addition to these compounds (**1**–**13**) we detected two very similar substances with the same formula $C_{10}H_{12}O$ (M^+ at *m/e* 148), which could not be completely identified by MS. After isolation by SC and prep. TLC the structures of **14** and **16** were elucidated by spectroscopic methods.

The presence of aromatic aldehydes was indicated by the IR spectra and confirmed by MS fragmentation patterns (strong peaks at M^+ and $M^+ - 1$) and NMR data. The 250 MHz ^1H NMR spectra of both the aldehydes displayed three singlets at 2.2, 2.4, 2.5 ppm and 2.2, 2.3, 2.6 ppm respectively, the ^{13}C NMR spectra three quartets at 15.3, 19.8, 20.1 ppm and 14.6, 15.1, 21.4 ppm respectively, representing three methyl groups on the aromatic ring. The coupling parameters of the remaining two ring protons ($I_{5,6} = I_{4,5} = 7.7$ Hz) indicated vicinal positions for both molecules. Considering all the NMR data, the structures of **14** and **16** were deduced (Table 2).

Compounds **15** and **17** were present in traces in freshly distilled oil. They increased in amount during storage and the simultaneous decrease of the aldehydes suggested **15** and **17** to be oxidation products of **14** and **16**. Their spectra were identical with those of the corresponding carboxylic acids.

DISCUSSION

A comparison of the composition of the essential root oil from *M. peloponnesiacum* with oils of other Apiaceae reveals significant differences. Only few of the Apiaceae contain 3-carene in large amounts. A comparable high content (30%) has only been found in *Platysace linearifolia* [4]. The aromatic aldehydes **14** and **16** have not yet been detected in essential oils.

However, Bohlmann and Zdero obtained **14** after acid treatment from a ferulol ester found in *Ferula hispanica* [5]. Therefore it has to be considered that this compound and the isomeric aldehyde **16** are produced

* Part 7 in the series "On the Essential Oils from the Apiaceae". For Part 6 see Stahl, E. und Kubeczka, K.-H. (1979) *Planta Med.* **37**, 49.

Table 1. Components of *Molopospermum peloponnesiacum* root oil

No.	Compounds	Percentages*	Identification
1	α-Pinene	4.5	MS, IR
2	Camphene	<0.1	MS
3	β-Pinene	<0.1	MS
4	Sabinene	0.3	MS
5	3-Carene	46.3	MS, IR, NMR
6	α-Phellandrene	1.9	MS
7	Limonene	2.7	MS
8	β-Phellandrene	2.2	MS
9	*p*-Cymene	1.0	MS
10	Terpinolene	1.7	MS
11	Thymol methyl ether	0.9	MS, IR, NMR
12	β-Selinene	1.4	MS, IR, NMR
13	β-Bisabolene	0.7	MS, IR
14	2,3,4-Trimethylbenzaldehyde	9.2	MS, IR, NMR
15	2,3,4-Trimethylbenzoic acid	traces	MS, IR, NMR
16	2,3,6-Trimethylbenzaldehyde	19.8	MS, IR, NMR
17	2,3,6-Trimethylbenzoic acid	traces	MS, IR, NMR

* Percentages are based on computer calculated area normalization. Percentages total 94.7.

during steam distillation from corresponding ferulol and isoferulol derivatives. A comparison of a fresh extract and the distillate from *Molopospermum* roots has finally confirmed this assumption. Compounds **14** and **16** were not detected in fresh extract, whereas the steam distillate of this extract contained a significant amount of both compounds. **14** and **16** are therefore artefacts, produced during steam distillation from ferulol and isoferulol esters by saponification and proton-catalyzed rearrangement.

Since ferulol and isoferulol esters have been found in fifteen genera of the Apiaceae, it has to be expected that **14** and **16** occur in steam distillates of numerous

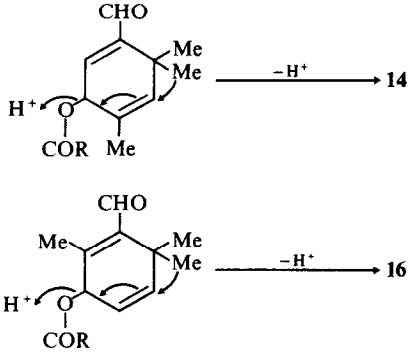


Table 2. ^{1}H and ^{13}C NMR parameters of components **14** and **16***

1H	14	16	^{13}C	14	16
2-Me	2.2 *s*	2.3 *s*	C-1	133.5 *s*	132.8 *s*
3-Me	2.4 *s*	2.6 *s*	C-2	138.7 *s*	138.8 *s*
4-Me	2.5 *s*	—	C-3	138.0 *s*	136.6 *s*
H-4	—	7.5 *d*	C-4	135.6 *s*	127.6 *d*
H-5	7.2 *d*	7.1 *d*	C-5	128.9 *d*	129.6 *d*
H-6	7.0 *d*	—	C-6	134.2 *d*	143.0 *s*
6-Me	—	2.2 *s*	2-Me	15.3 *q*	15.1 *q*
CHO	10.6 *s*	10.2 *s*	3-Me	19.8 *q*	21.4 *q*
			4-Me	20.1 *q*	—
			6-Me	—	14.6 *q*
			CHO	194.5 *d*	192.8 *d*

J (Hz): 5.6 = 7.7; 4.5 = 7.7.

* Spectra were run in C_6H_6 at 250 MHz (^{1}H NMR) and 62.9 MHz (^{13}C NMR), respectively, TMS as internal standard.

Umbelliferae. The genera reported to contain these derivatives—*Anthriscus* (Kubeczka, K. H., unpublished results), *Astrantia, Bupleurum, Cenolophium, Cnidium, Eryngium, Ferula, Hacquetia, Hladnikia, Ligusticum, Peucedanum, Selinum, Seseli, Silaum, Silaus* (Bohlmann, F., personal communication)—belong to different tribes of the Apiaceae. Since the remaining components of the root oil of *M. peloponnesiacum* are not taxon specific, the present results are not of chemosystematic significance.

EXPERIMENTAL

GC–MS. Finnigan System 3200, 50 m PEG WCOT glass capillary column, linear temperature programme (70–200°; 2.5°/min), 1.5 ml He/min; 70 eV. ^{1}H NMR (250 MHz) and ^{13}C NMR (62.9 MHz) spectra were measured in C_6D_6 soln. Chemical shifts are shown in δ values relative to internal TMS.

Plant material and isolations. The roots of flowering plants were collected on Mt. Baldo, Italy in June 1979. A voucher specimen is deposited in the authors' herbarium. The essential oil was obtained from chopped fresh roots by steam distillation with a receiver, as used by the European Pharmacopoeia for determination of volatile oil in drugs. The pale yellow oil (yield 3.24% of dry weight; $d_{20}^{20} = 0.9239$; $n_D^{20} = 1.5046$) was separated by GLC. The main substances were isolated individually by column chromatography using Si gel (Woelm); development with pentane and increasing amounts of Et_2O. Repeated chromatography of the hydrocarbon fraction with Si gel–pentane at −20° [6] yielded pure 3-carene, which was identical with an authentic sample. The more polar fractions were separated by prep. TLC (Si gel HF_{254}, 0.5 mm, C_6H_{14}–$CHCl_3$, 1:1). They yielded **14** (R_f 0.61) and **16** (R_f 0.47).

2,3,4-*Trimethylbenzaldehyde* **14**. Pale yellowish oil. $C_{10}H_{12}O$ (M^+ at *m/e* 148). IR_{max}^{film} cm^{-1}: 3050, 2755, 1685, 1570, 1378, 810. MS *m/e* (rel. int.): 147 (100), 148 (92), 119 (91), 105 (36), 91 (30), 77 (22). ^{1}H and ^{13}C NMR data see Table 2.

2,3,6-*Trimethylbenzaldehyde* **16**. Pale yellowish oil. $C_{10}H_{12}O$ (M^+ at *m/e* 148). IR_{max}^{film} cm^{-1}: 3050, 2715, 1673, 1590, 1237, 1218, 810, 772, 762. MS *m/e* (rel. int.): 147 (100), 148 (79), 119 (66), 91 (34), 105 (32), 121 (30). ^{1}H and ^{13}C NMR data see Table 2.

Acknowledgements—We thank Dr. V. Formacek, Bruker Physik AG, Rheinstetten (Germany) for NMR spectroscopy and Miss A. Viernickel, Institut für Botanik und Pharmazeutische Biologie, Würzburg for technical assistance. One of us (I.U.) is indebted to the Deutsche Forschungsgemeinschaft for financial support.

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