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4,5-EPOXY-*p*-MENTH-1-ENE: A NEW CONSTITUENT OF *ORIGANUM HERACLEOTICUM**

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Key Word Index—*Origanum heracleoticum*; Labiatae; essential oil; 4,5-epoxy-*p*-menth-1-ene; monoterpene epoxide.

Origanum heracleoticum L., which is a plant native to Greece, is used in large quantities throughout the world as the condiment Greek Oregano. Unfortunately, much confusion exists in the world today on the correct taxonomic classification of oregano.[1] For example, the following plants have been referred to as oregano: *O. vulgare* L., *O. gracile* L., *O. glandulosum* Link., *O. smyrnicum* L., *O. syriacum* (≡ *O. maru* L., *Marjorana maru* (L.)Briq.), *O. onites* Benth., *O. virens* Hoffm. et Link, *Coridothymus capitatus* Rchb., *Lippia graveolens* H.B.K., various *Lippia* species, etc.

The chemical composition of *O. heracleoticum* has received some attention and the presence of carvacrol,[3–6] thymol,[4–6] borneol,[3,4,6] linalool,[3,4,6] camphor,[3,6] amyl alcohol,[3,4] bornyl acetate,[3] terpinen-4-ol,[4] 1,8-cineole,[4] carvone,[4] β-bisabolene,[4] caryophyllene[4] and a number of monoterpene hydrocarbons[3,4,6] (including δ-terpinene[4]) have been reported.

During a recent routine analysis[6] of the essential oil of *O. heracleoticum*, an unusual compound was isolated. It is the purpose of this note to describe its structural elucidation and synthesis.

RESULTS AND DISCUSSION

From the IR and retention time (on Carbowax 6000) of the unknown constituent isolated from a medium boiling fraction of the oil, it could be misinterpreted that the compound was a sesquiterpene hydrocarbon. This conclusion can be readily proven incorrect from MS ($M^+ = 152$) and NMR (16 protons) which show that the molecular formula must be $C_{10}H_{16}O$. The NMR data given in Table 1 is consistent with structure **1**. To prove this, 4,5-epoxy-*p*-menth-1-ene (**1**) was synthesized from γ-terpinene (**2**) using monoperphthalic acid.[7] It is interesting to note that only one major product results from epoxidation

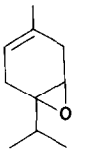
* Part XIV in the series "Essential Oils and Their Constituents". For Part XIII see *Flavour Industry* in press (1974).

[1] CALPOUZOS, L. (1954) *Econ. Bot.* **8**, 222.
[2] STAIKOV, V., ZOLOTOVICH, G. and KALAIDZHIEV, I. (1968) *Soap Perfum. & Cosmet.* **41**, 327.
[3] CALZOLARI, C., STANCHER, B. and PERTOLDI MARLETTA, G. (1968) *Analyst* **93**, 311.
[4] TANKER, M. (1965) *Istanbul Ecz. Fak. Mec.* **1**, 32.
[5] SKRUBIS, B. G. (1972) *Flavour Industry* **3**, 566.
[6] LAWRENCE, B. M. (1972) unpublished results.
[7] VOGL, A. I. (1959) *Practical Organic Chemistry*, 3rd Edn, p. 810, Longmans, London.

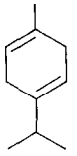
TABLE 1. NMR SPECTRAL DATA FOR 4,5-EPOXY-*p*-MENTH-1-ENE

δ	No. of protons	Type	J (Hz)	Interpretation
0·945	6	2d	7	$(CH_3)_2$–CH–
1·48	1	sept.	7	–C–CH–$(CH_3)_2$
1·85	3	b.s.	—	CH_3–C=CH–
2·30	4	v.b.s.	—	2 equivalent $-CH_2-$
2·85	1	b.s.	—	CH–O–
5·09	1	b.s.	—	CH=C

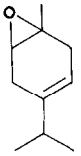
whereas one might expect that both epoxides **1** and **3** could be formed under the conditions used. To our knowledge this is the first time that an epoxide of γ-terpinene has been found naturally occurring.



(1)



(2)



(3)

EXPERIMENTAL

Isolation and purification. After steam distillation of *Origanum heracleoticum*, the oil (2·4%) was analysed using methods described previously.[8] From a medium boiling fraction, an unknown constituent was isolated from the oxygenated constituents. The compound was purified using preparative GC over Carbowax 6000.

Spectroscopy. The IR spectrum of **1**, which was run on a thin film (0·013 mm spacer), showed characteristic absorptions at 865, 880, 1450, 1365, 1385, 1422, 1030, 1048, 1080, 1228, 1308 cm^{-1}. The NMR was run as a 1% soln in $CDCl_3$ using a Varian Aerograph 220 MHz spectrometer. The MS was run on a Varian Aerograph EM 600 Mass Spectrometer using an internal standard of mixed alkyl benzenes.

[8] LAWRENCE, B. M. (1971) *Can. Instit. Food Technol. J.* **4**, 444.