Phytochemistry, Vol. 25, No. 5, pp. 1223–1224, 1986.
Printed in Great Britain.

0031-9422/86 \$3.00 + 0.00

ISOMERIC EPOXIDES OF MATRICARIA ESTER FROM *ERIGERON PHILADELPHICUS*

J. JAKUPOVIC, T. N. CHAU-THI and N. H. FISCHER*

Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, West Germany; *Department of Chemistry, The University of Louisiana, Baton Rouge, LA 70803, U.S.A.

(*Received* 20 *August* 1985)

Key Word Index—*Erigeron philadelphicus*; Compositae; acetylenes; epoxides of matricaria ester.

Abstract—The aerial parts of *Erigeron philadelphicus* afforded in addition to widespread compounds and known acetylenes the isomeric epoxides of matricaria ester. The structure of one of these was established by partial synthesis.

INTRODUCTION

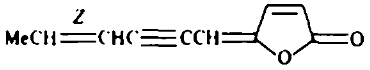
Previous investigations of *Erigeron philadelphicus* L. (tribe Astereae) afforded lachnophyllum ester, matricaria ester [1] and a labdane derivative [2]. We now have studied a sample collected in Louisiana. In addition to widespread compounds (see Experimental) the aerial parts gave the acetylenic compounds **1** [3], **2** [3], **3** [4], **4** [5], and two new ones, the isomeric epoxides **5** and **6**. The structures of **5** and **6** were deduced easily from the molecular formula ($C_{11}H_{10}O_3$) and from the ^1H NMR spectrum (see Experimental). As the concentrations of the isomers were different (*ca* 2:1) all signals could be assigned by spin decoupling. The UV spectrum is of course close to that of lachnophyllum ester [6]. Furthermore **5** was obtained by reaction of **1** with *m*-chloroperbenzoic acid. Accordingly, the configuration at C-8 and C-9 of isomer **5** was established and consequently **6** was the *trans*-isomer. Compounds **5** and **6** are the first natural occurring epoxides of matricaria ester. The 10-acetoxy derivative of **5** has been isolated from *Chrysothamnus* species, also of the tribe Astereae [7].

EXPERIMENTAL

The air dried aerial parts (300 g, collected in April 1985, East Baton Rouge Parish, Louisiana, U.S.A.) were extracted with Et_2O–MeOH–petrol (1:1:1), and the extract obtained was separated first by CC (silica gel) and further by prep. TLC (silica gel, PF 254). The non-polar CC fractions (petrol and Et_2O–petrol, 1:10) gave 30 mg *β*-farnesene, 10 mg bisabolene, 5 mg squalene, 4 mg **4**, 100 mg **1** and 5 mg **2**. The CC fraction obtained with Et_2O–petrol (1:3) afforded by prep. TLC (C_6H_6–CH_2Cl_2, 1:1) 10 mg **5** and **6** (*ca* 2:1, R_f 0.7). The CC fraction obtained with Et_2O–petrol (1:1), gave by prep. TLC (Et_2O–petrol, 2:3) 12 mg **3**, 5 mg cycloartenone and 10 mg erythrodiol. Known compounds were identified by comparing

$\mathrm{MeCH{=}CH[C{\equiv}C]_2CH{=}CHCO_2Me}$

1 *ZZ*
2 *ZE*



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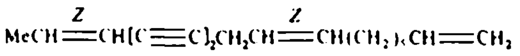
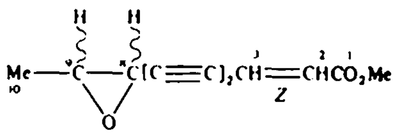


$\mathrm{Me}\overset{Z}{\mathrm{CH{=}CH}}\mathrm{[C{\equiv}C]_2CH_2}\overset{Z}{\mathrm{CH{=}CH}}\mathrm{(CH_2)_5CH{=}CH_2}$

4



5 8,9-*cis*
6 8,9-*trans*

Table 1. ^{1}H NMR spectral data of **5** and **6** (400 MHz, $CDCl_3$, TMS as internal standard)

H	**5**	**6**
2	6.28 *d*	6.27 *d*
3	6.18 *dd*	6.16 *dd*
8	3.55 *dd*	3.20 *br d*
9	3.24 *dq*	3.23 *dq*
10	1.45 *d*	1.36 *d*
OMe	3.78 *s*	3.77 *s*

J (Hz): 2,3 = 11; 9,10 = 5; compound **5**: 3,8 = 0.7; 8,9 = 4; compound **6**: 3,8 ~ 0.5; 8,9 = 2.

the 400 MHz ^{1}H NMR spectra with those of authentic material.

Epoxides of matricaria ester (**5** *and* **6**). Colourless oil; UV $\lambda_{max}^{Et_2O}$ nm: 304, 287, 270, 210; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2240, 2160 (C≡C), 1720, 1610 (C=CCO$_2$R); MS *m/z* (rel. int.): 190.063 (5) $[M]^+$ (calc. for $C_{11}H_{10}O_3$: 190.063), 175 (6) $[M-Me]^+$, 159 (12) $[M-OMe]^+$, 146 (15) $[M-C_2H_4O]^+$, 131 (100) $[159-CO]^+$. 20 mg *Z,Z*-matricaria ester were heated for 3 hr in 5 ml $CHCl_3$ with 40 mg *m*-chloroperbenzoic acid. TLC of the reaction products gave 8 mg **5**, identical with the natural product (^{1}H NMR and TLC).

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Phytochemistry, Vol. 25, No. 5, pp. 1224–1226, 1986.
Printed in Great Britain.

0031 9422/86 $3.00 + 0.00

(*E*)-9-CHLORO-8-NONENE-4,6-DIYNE-1,2,3-TRIOL, AN ARTEFACT FROM *PNEUMATOSPORA OBCORONATA*

D. H. G. Crout, P. J. Fisher*, V. S. B. Gaudet, H. Stoeckli-Evans† and Avril E. Anson*

Department of Chemistry, University of Warwick, Coventry, CV4 7AL, U.K.; *Department of Biological Sciences, Hatherly Laboratories, University of Exeter, Exeter EX4 4PS, U.K.; † Université de Neuchâtel, Institut de Chimie, Av. de Bellevaux 51, CH-2000 Neuchâtel, Switzerland

(*Revised received* 23 *September* 1985)

Key Word Index—*Pneumatospora obcoronata*; hyphomycete; polyacetylene; artefact.

Abstract—A hyphomycete, Exeter Herbarium Number 23000, was isolated in Malaysia from green leaves of the fruit tree *Nephelium lappaceum* (rambutan) and from fallen leaves of *Hevea brasilienisis* (rubber). The fungus was grown for five days in a malt extract medium. From the mycelial filtrate, a novel compound, (*E*)-9-chloro-8-nonene-4,6-diyne-1,2,3-triol, was extracted.

INTRODUCTION

Pneumatospora obcoronata is a species of a newly-described genus found among the mycoflora of fruit tree leaves in Malaysia [1]. Extraction of cultures of the organism with ethyl acetate gave material which, although relatively stable in solution, rapidly polymerized on evaporation of the solvent to a dark-coloured, largely insoluble crystalline material. The portion of the evaporated material soluble in methanol was subjected to prep. TLC and HPLC to give a colourless compound for which structure **1** is proposed on the basis of the following evidence.

RESULTS AND DISCUSSION

An accurate mass determination indicated a molecular formula of $C_9H_9O_3Cl$. This was supported by the in-