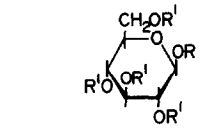
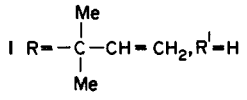
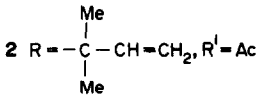




1 R = –C(Me)$_2$–CH=CH$_2$, R^1 = H



2 R = –C(Me)$_2$–CH=CH$_2$, R^1 = Ac

3 R = –C(Me)$_2$–CH$_2$–Me, R^1 = H

4 R = –C(Me)$_2$–CH$_2$–Me, R^1 = OAc

Tetraacetyl-dihydro-derivative (**4**). Treatment of **3** with Ac_2O/Py as **1** gave **4**.. mp 120–121° (Et_2O–pentane); $[\alpha]_D^{24°}$ −10° (*c* 0.94; $CHCl_3$); ν_{max}^{KBr} 1755, 1370, 1240 cm^{-1}; NMR ($CDCl_3$): δ 5.30–4.80 (H-2′, 3′, 4′, *m*), 4.65 (H-1′, *d*, $J_{1',2'}$ 8.0 Hz), 4.23 (H-6′$_{1,a}$, $J_{6'_1,6'_2}$ 12.0, $J_{6',5}$ 5,5 Hz), 4.06 (H–6′$_2$, *q*, $J_{6'_2,5}$ 2.7 Hz), 3.68 (H-5′, *m*, $J_{4',5'}$ 9.0, $J_{5',6'_1}$ 5.5, $J_{5',6'_2}$ 2.7 Hz), 2.03 (3H, *s*, OAc), 2.00 (6H, *s*, 2OAc), 1.97 (3H, *s*, -OAc), 1.48 (2H-3, *q*, *J* 6 Hz, Me–CH_2–) 1.18 and 1.16 (2Me, 2*s*), and 0.86 (3H, *t*, CH_3–CH_2–). (Found: C 54.23; C 54.23; H 6.93, $C_{19}H_{30}O_{10}$ requires: C 54.53; H 7.23%.

Synthesis of **4**. Drierite (2 g), yellow mercuric oxide (0.8 g), mercuric bromide (0.05 g), abs. $CHCl_3$ and 2-methyl-2-butanol (5 ml) were stirred for 0.5 hr. 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (1.8 g) was added and stirring continued for 24 hr. After the usual work up **4** (1.7 g) was obtained, mp 120–121°; $[\alpha]_D^{24°}$ −10° (*c* 1.02; $CHCl_3$). This compound was identical with an authentic sample of **4** (mmp, TLC,1 IR (KBr), NMR ($CHCl_3$).

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EPOXYOCTADECADIENOIC ACIDS FROM *CREPIS CONYZAEFOLIA* SEED OIL

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Key Word Index—*Crepis conyzaefolia*; Compositae; seed oil; vernolic acid, epoxy fatty acids; PMR; ORD; GC–MS; ozonolysis.

Abstract—The seed oil of *Crepis conyzaefolia* (Gouan) Dalle Torre contains previously unidentified (±)-*cis*-12,13-epoxyoctadeca-*trans*-6-*cis*-9-dienoic (14%) and *cis*-12,13-epoxyoctadeca-*cis*-6-*cis*-9-dienoic (2%) acids and the more common vernolic [(±)-12,13-epoxyoctadec-*cis*-9-enoic] (32%) acid.

INTRODUCTION

The presence of unusual fatty acids in *Crepis* seeds was first noticed by Mikolajczak *et al.* who characterized crepenynic (octadec-*cis*-9-en-12-ynoic) acid from *C. foetida* [1]. Later, Tallent and coworkers found vernolic [(±)-*cis*-12,13-epoxyoctadec-*cis*-9-enoic] acid as a major constituent in the seed oils from five *Crepis* species [2]. Earle, in his review of the occurrence of epoxy acids in seeds, recognized three categories of *Crepis* oils, "one group of species rich in vernolic acid, another rich in crepenynic acid and a third group intermediate in composition" [3]. As a variant of the vernolic acid group, *C. conyzaefolia* contains vernolic and two previously unknown acids: (±)-*cis*-12,13-epoxyoctadeca-*trans*-6-*cis*-9-dienoic and *cis*-12,13-epoxyoctadeca-*cis*-6-*cis*-9-dienoic.

RESULTS AND DISCUSSION

The *C. conyzaefolia* seeds contained 36.7% oil (dry basis). Me esters prepared from the oil had the composition shown in Table 1.

Immediately obvious by GLC were two components slightly more polar than Me vernolate on the polyester

Table 1. Fatty acid composition of *Crepis conyzaefolia* oil as Me esters)

Component	Area % by GLC*
12:0	tr
13:0	tr
14:0	0.1
15:0	tr
16:0	3.1
16:1	0.2
17:0	tr
17:1	tr
18:0	1.4
18:1	25
18:2	19
18:3	0.9
20:0	0.3
22:0	0.1
Crepenynate	1.2
Epoxystearate	0.6
Vernolate	32
c,c-Epoxydienoate	2.1
t,c-Epoxydienoate	14

* tr denotes component was detected in an amount too small to quantitate.

column. They had ECL values [4] of 23.4 and 23.5, indicative of epoxydienoates. Me vernolate gave an ECL of 23.0 under identical conditions. Also striking was the presence of *trans* unsaturation in the oil and in its Me esters revealed by a medium intensity IR band at 970 cm^{-1}.

The epoxy esters isolated by either column chromatography or HPLC on μ-Porasil continued to show these characteristics. Nonoxygenated esters contained no *trans* unsaturation and the ECL values of the C_{18} unsaturated esters gave no indication of unusual isomers [4]. The epoxy esters were separated into three components by HPLC on the μ-Bondapak columns. These three esters were identified as **1**, **2** and **3** below; the small amount of epoxystearate present was eluted with the vernolate.

Epoxydienoate **1**

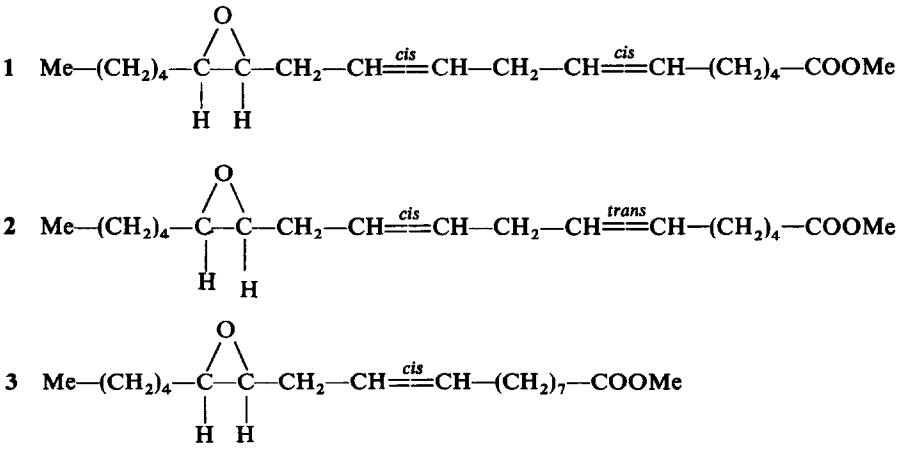
This ester had ECL values of 19.3 (Apiezon L) and 23.4 (LAC-2-R 446) and its IR spectrum showed no *trans* unsaturation. A M^+ at *m/e* 308 indicated a C_{18} Me ester with an additional oxygen atom and three rings and/or double bonds. The PMR spectrum, consistent with structure **1**, had the following features (100 MHz, $CDCl_3$): δ0.9 (3H, *t*, C-18), δ1.25–1.65 (12H, *m*, C-14 to C-17, C-3 and C-4), δ2.0 (4H, *m*, C-5 and C-11), δ2.3 (2H, *t*, C-2), δ2.75 (2H, *m*, C-8), δ2.88 (2H, *m*, C-12 and C-13 [5]), δ3.64 (3H, *s*, OOMe), δ5.28–5.64 (4H, *m*, C-6, C-7, C-9 and C-10). Ozonolysis followed by GC–MS gave only two components: a 6-carbon aldehyde-ester (AE) and a 9-carbon epoxyaldehyde (EA). Treatment of **1** with BF_3–MeOH and GC–MS of the silylated product [6] proved that the epoxy group was in the 12,13 position. Therefore, the structure of ester **1** is established.

Epoxydienoate **2**

ECL values for this ester were 19.3 (Apiezon L) and 23.5 (LAC-2-R-446). Its MS was identical to that of ester **1** and its PMR spectrum differed only in the shape of the olefin multiplet. A strong band for *trans* unsaturation (970 cm^{-1}) was evident in its IR spectrum. After the position of the epoxy group had been ascertained as in **1** above, this ester was ozonized and it, too, yielded a 6-carbon AE and a 9-carbon EA. ORD values for this ester ($[\alpha]_D$ +1.2°, $[\alpha]_{550}$ +1.2°, $[\alpha]_{500}$ +1.3°, $[\alpha]_{450}$ +1.2°, $[\alpha]_{400}$ +0.7° and $[\alpha]_{350}$ −1.2°) gave a plot similar in shape to that obtained from Me vernolate [7]. Reduction with hydrazine gave three products (a *cis*- and a *trans*-epoxymonoene and epoxystearate) plus unreacted starting material. The epoxymonoenes, almost completely resolved by HPLC (μ-Bondapak), eluted closely together with the *trans* isomer preceding the *cis* as evidenced by their PMR and IR spectra. Ozonolysis gave a 6-carbon AE and a 12-carbon EA from the *trans* component and a 9-carbon AE and EA from the *cis*, thereby establishing the structure of ester **2**.

Epoxymonoenoate **3**

ECL values and IR, MS and PMR of this ester were identical to those of authentic Me vernolate. Their ORD curves were superimposable [7]. Ozonolysis of **3** gave only the 9-carbon AE and EA. The epoxy group was located as in **1** and **2** above.



EXPERIMENTAL

Chromatography. Me-esters were analyzed by GLC as previously described [8]. For GC–MS, columns and conditions were essentially the same except when ozonolysis products were analyzed. In these instances, a precolumn containing palladium chloride was used with H_2 as the carrier gas [9, 10]. Initially, the catalyst reduced components to their carbon skeletons; however, injection of 5–10 μl of CS_2 adjusted the catalyst activity so that ozonides were reduced to aldehydes. HPLC was carried out on a preparative scale (25 mg injections) with the following columns and solvent systems: μ-Porasil, 1 ft × ¼ in. OD, and hexane–Et_2O (9:1); μ-Bondapak C_{18}, 2 (1 ft × ¼ in. OD) (Waters Assoc.), and MeOH–H_2O (3:1). For column chromatography, a 50 × 1.5 cm column was packed with 25 g of 60–200 mesh Hi-Flosil. Esters (*ca* 2 g total) were eluted with 1 l. hexane followed by 1 l. of hexane–Et_2O (9:1).

Spectral analysis. For GC–MS, the GC was coupled to the MS through a jet-type separator. The computerized data acquisition–reduction system has been detailed elsewhere [11]. PMR spectra were measured in $CDCl_3$ and IR spectra in CS_2. To permit comparison with the data of ref [7], ORD curves were obtained as hexane solns.

Sample preparation. Oil was extracted from the ground seeds with petrol (bp 35–60°), and the Me esters prepared by NaOMe transesterification [12]. Hydrazine reduction was carried out in EtOH [5]. Samples were ozonized in CH_2Cl_2 [13] and injected directly into the GC–MS system without the addition of triphenylphosphine. For location of epoxy groups, derivatives were prepared by treatment with BF_3/MeOH followed by silylation [6].

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LES MONOTERPENES DE *CONOCEPHALUM CONICUM, FRULLANIA TAMARISCI* ET *PORELLA PLATYPHYLLA**

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Key Word Index—*Conocephalum conicum*; *Frullania tamarisci* ssp. *tamarisci*; *Pellia epiphylla*; *P. fabbroniana* f. *furcigera*; *Porella platyphylla*; Hepaticae (liverworts); Bryophytes; essential oil; monoterpenes.

Des sesquiterpènes ont été mis en évidence dans les essences extraites de nombreuses Hépatiques [1]; des monoterpènes n'ont été identifiés que chez cinq espèces [2–5], dont *Conocephalum conicum* [3].

Conocephalum conicum (L.) Dum. (Marchantiale), *Pellia epiphylla* (L.) Corda et *P. fabbroniana* Raddi f. *furcigera* (Hook.) Mass, (Metzgériales), *Frullania tamarisci* (L.) Dum. ssp. *tamarisci* Hatt. et *Porella platyphylla* (L.) Lindb. (Jungermanniales) ont été récoltés dans le SW de la France (Dordogne, Gironde). Des échantillons ont été déposés dans l'Herbier de Bryophytes du Museum National d'Histoire Naturelle, Laboratoire de Cryptogamie, 12 rue de Buffon, 75005 Paris, France.

Les échantillons (100–200 g poids frais) sont triés, lavés et séchés 24 hr à température ambiante, puis broyés en présence de *n*-pentane distillé, chromatographiquement pur. Après 48 hr de macération à l'abri de la lumière, l'extrait (environ 1 l) est chromatographié sur colonne d'alumine neutre (150 g). La fraction éluée par le pentane (2 l) est conc. puis étudiée par GC–MS. Les monoterpènes sont identifiés par comparaison de leurs spectres de

* Note 4 de la série 'Les essence extraites du thalle des Hépatiques', 3: *Rev. Bryol. Lichénol.* (à paraître).