EPOXYOCTADECADIENOIC ACIDS FROM CREPIS CONYZAEFOLIA SEED OIL

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

Abstract—The seed oil of Crepis conyzaeifolia (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-epoxyoctadeca-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-eis-9-en-12-yinoic) acid from C. foetida [1]. Later, Tallent and coworkers found vernolic [(±)-cis-12,13-epoxyoctadeca-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. conyzaeifolia 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. conyzaeifolia 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

<table>
<thead>
<tr>
<th>Component</th>
<th>Area % by GLC</th>
</tr>
</thead>
<tbody>
<tr>
<td>12:0</td>
<td>tr</td>
</tr>
<tr>
<td>13:0</td>
<td>tr</td>
</tr>
<tr>
<td>14:0</td>
<td>0.1</td>
</tr>
<tr>
<td>15:0</td>
<td>tr</td>
</tr>
<tr>
<td>16:0</td>
<td>3.1</td>
</tr>
<tr>
<td>16:1</td>
<td>0.2</td>
</tr>
<tr>
<td>17:0</td>
<td>tr</td>
</tr>
<tr>
<td>17:1</td>
<td>tr</td>
</tr>
<tr>
<td>18:0</td>
<td>1.4</td>
</tr>
<tr>
<td>18:1</td>
<td>25</td>
</tr>
<tr>
<td>18:2</td>
<td>19</td>
</tr>
<tr>
<td>18:3</td>
<td>0.9</td>
</tr>
<tr>
<td>20:0</td>
<td>0.3</td>
</tr>
<tr>
<td>22:0</td>
<td>0.1</td>
</tr>
<tr>
<td>Crepenynate</td>
<td>1.2</td>
</tr>
<tr>
<td>Epoxydieneate</td>
<td>0.6</td>
</tr>
<tr>
<td>Vernolate</td>
<td>32</td>
</tr>
<tr>
<td>t.c-Epoxydieneate</td>
<td>2.1</td>
</tr>
<tr>
<td>c.c-Epoxydieneate</td>
<td>14</td>
</tr>
</tbody>
</table>

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

unsaturation. A M⁻ at *m/z* 308 indicated a C₁₈ 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, CDCl₃): δ 0.9 (3H, t, C-18), δ 1.25–1.65 (12H, m, C-14 to C-17, C-3 and C-4), δ 2.0 (4H, m, C-5 and C-11), δ 2.3 (2H, t, C-2), δ 2.75 (2H, m, C-8), δ 2.88 (2H, m, C-12 and C-13 [5]), δ 3.64 (3H, s, OOMe), δ 5.28–5.64 (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 BF₃-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.

Epoxydieneate 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 ([α]D +1.2°, [α]550 +1.2°, [α]450 +1.2°, [α]350 +0.7° and [α]300 −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 of 3 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 H₂ as the carrier gas [9, 10]. Initially, the catalyst reduced compounds to their carbon skeletons; however, injection of 5–10 μl of CS₂ 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-Porisil 1 ft x 0.1 in. OD, and hexane–Et₂O (9:1); μ-Bondapak (Waters Assoc.) 2 ft x 0.1 in. OD. For column chromatography, a 50 × 1.5 cm column was packed with 25 g of 60–200 mesh Hi–FLO SI. Esters (ca 2 g total) were eluted with 1 L hexane followed by 1 L of hexane–Et₂O (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 CDCl₃ and IR spectra in CS₂. To permit comparison with the data of ref [7], ORD curves were obtained in CDCl₃ and IR spectra in CS₂. For column chromatography, a 50 × 1.5 cm column was packed with 25 g of 60–200 msh Hi–FLO SI. Esters (ca 2 g total) were eluted with 1 L hexane followed by 1 L of hexane–Et₂O (9:1).

Sample preparation. Oil was extracted from the ground seeds with petrol (bp 35–60°C), and the Me esters prepared by NaOMe transesterification [12]. Hydrazine reduction was carried out in EtOH [5]. Samples were ozonized directly into the GC–MS system without the addition of tripheylphosphine. For location of epoxy groups, derivatives were prepared by treatment with BF₃/MEOH followed by silylation [6].

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REFERENCES

Purchased by Agricultural Research Service
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LES MONOTERPENES DE CONOCEPHALUM CONICUM, FRULLANIA TAMARISCET ET PORELLA PLATYPHYLLA*

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Key Word Index—Conocephalum conicum; Frullania tamariscet ssp. tamariscet; Pellia epiphyllia; P. fabbroniana f. furcigera; Porella platypyllia; Hepaticae (liverworts); Bryophytes; essential oil; monoterpenes.

Des sesquiterpènes ont été mis en évidence dans les essences extraites de nombreuses Hepaticas [1]: des monoterpenes n’ont été identifiés que chez cinq espèces [2–5], dont Conocephalum conicum [3].


Les échantillons (100–200 g poids frais) sont triés, lavés et séchés 24 h à température ambiante, puis broyés en présence de n-pentane distillé, chromatographiquement pur. Après 48 h de macération à l’abri de la lumière, l’extrait (environ 11) est chromatographié sur colonne d’alumine neutre (150 g). La fraction élue par le pentane (2 l) est conc. puis étudiée par GC–MS. Les monoterpenes sont identifiés par comparaison de leurs spectres de