product of the LAP reaction (apart from amino acid products, serine and homoarginine) was identical to the corresponding product obtained by the action of LAP on phaseolotoxin: thus it is N^δ-phosphosulphamyl ornithine. Standard *N*-terminal analysis with 2,4-dinitrofluorobenzene showed that the ornithyl residue of **1** was *N*-terminal and δ-substituted.

Together these data supply sufficient information to establish the structure of compound **1**. In the peptide portion, ornithine is *N*-terminal and homoarginine is *C*-terminal, so that the amino acid sequence must be ornithine-serine-homoarginine. This is as in phaseolotoxin, but with serine replacing alanine. The ornithine is N^δ-substituted, and the substituent group is sulphamyl phosphate. Thus **1** is (N^δ-phosphosulphamyl) ornithithylserylhomoarginine (**1**); compound **2** is ornithylserylhomoarginine (**2**) and compound **3** is (N^δ-phosphosulphamyl) ornithylserine (**3**).

The new toxin is thus a serine analogue of phaseolotoxin. There is good evidence that tabtoxin, the toxin of *Ps. tabaci* and other *Pseudomonas* species, also has a serine analogue, and the name [2-serine]-tabtoxin has already been given to this compound [4, 5]. In keeping with this useful terminology we propose the name [2-serine]-phaseolotoxin for the minor toxin of *Ps. phaseolicola.*

EXPERIMENTAL

All procedures used have been previously described [1].

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2-METHYL-3-BUTEN-2-YL-β-D-GLUCOPYRANOSIDE FROM *FERULA LOSCOSII*

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Key Word Index—*Ferula loscosii*; Umbelliferae; 2-methyl-3-buten-2-yl-β-D-glucopyranoside.

Ferula loscosii (Lge.) Wk. (*Elaeoselinum loscosii* Lge.)* is an endemic species in Spain (near Aranjuez and Chiprana, Teruel). From the aerial parts of this plant a new glucoside, $C_{11}H_{20}O_6$, (**1**) (0.8% of dry plant) has been isolated. Acid hydrolysis of **1** gave D-glucose and treatment of **1** with Ac_2O–Py afforded a tetraacetyl derivative (**2**). The 100 MHz NMR spectrum of **1** showed signals at δ 6.28 (1H), 5.28 (1H) and 5.03 (1H) for a $CH_2{=}CH{-}\underset{|}{\overset{|}{C}}{-}$ grouping; 1.43 (3H) and 1.37 (3H) for $(Me)_2C{<}$ and the expected signals for the D-glucopyranose moity between 4.78–3.50. The anomeric proton appeared as a doublet at 4.78 (*J* 8.0 Hz) indicative of β-configuration at the anomeric centre. The above data suggest formula **1** for this compound. On the other hand, hydrogenation of **1** gave **3**, a dihydro derivative, the NMR spectrum of which showed signals for Me–CH_2– at 0.95 and 1.62. The tetraacetyl derivative of **3** (compound **4**) was identical in all respects with the product obtained by a modified Koenigs–Knorr reaction [1] of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide with 2-methyl-3-buten-2-ol.

EXPERIMENTAL

Mp's are uncorrected. NMR spectra were recorded at 100 MHz. Plants were collected at Aranjuez (Madrid) in June 1974. Identified by Dr. J. Borja, Voucher specimens (No 90066) were deposited in the Herbarium, Faculty of Pharmacy (Ciudad Universitaria, Madrid).

Extraction and isolation of **1**. Dry aerial parts (800 g) were extracted first with ether-petrol (1:2) and then with MeOH in a Soxhlet. The methanolic extract (40 g) was introduced in a drypacked column of Si gel. Elution with $CHCl_3$ and $CHCl_3$–MeOH (100:3) gave crude **1** (10 g), rechromatography yielded pure **1** (6.5 g): mp 135–136° (Me_2CO); $[\alpha]_D^{20°}$ $-25°$ (*c* 1.07; Py); ν_{max}^{nujol} 3450 cm^{-1}; NMR (Py): δ 6.28 (H-3, *q*, $J_{3,4_1}$ 10.0, $J_{3,4_2}$ 18.0 Hz), 5.28 (H-4_2, *q*, $J_{4_2,3}$ 18, $J_{4_2,4_1}$ 2 Hz), 5.03 (H-4_1, *q*, $J_{3,4_1}$ 10.0, $J_{4_2,4_1}$ 2 Hz), 4.78 (H-1′, *d*, *J* 8 Hz), 4.50–3.50 (H-2′, 3′, 4′, 5′, and 2H-6′, *m*), 1.43 and 1.37 ($2CH_3$, 2*s*). MS: *m/e* 163(M^+-85). (Found: C 53.07; H 7.93. $C_{11}H_{20}O_6$ requires: C 53.21; H 8.12%).

Tetraacetyl-derivative (**2**). Ttreatment of compound **1** (100 mg) with Ac_2O–Py for 48 hr at room temp gave **2** (80 mg); mp 113–114° (Me_2CO/Hexane); $[\alpha]_D^{25°}$ $-6°$ (*c* 1.08; $CHCl_3$); ν_{max}^{KBr} 1760, 1745, 1380, 1258, 1225 cm^{-1}; NMR ($CDCl_3$): δ 5.84 (H-3, *q*, $J_{3,4_1}$ 10 and $J_{3,4_2}$ 17.5 Hz), 4.53 (H-1′, *d*, $J_{1',2'}$ 8.0 Hz), 4.20 (H-$6'_1$, *q*, $J_{5',6'_1}$ 5.5, $J_{6'_1,6'_2}$ 11.5 Hz), 4.04 (H-$6'_2$, *q*, $J_{5',6'_2}$ 2.5, $J_{6'_1,6'_2}$ 11.5 Hz), 3.62 (H-5′, *m*), 2.06, 2.08, 2.00, 1.98 (4 OAc·4*s*), 1.33 and 1.27 (2Me, 2*s*). MS: *m/e* 347(M^+-63). (Found: C 54.65; H 6.97. $C_{19}H_{28}O_{10}$ requires: C 54.80; H 6.78%).

Dihydro-derivative (**3**). **1** (100 mg) in EtOH with 10% Pd–C (40 mg) at room temp, gave **3**; mp 120–121° (MeOH–Et_2O); $[\alpha]_D^{20°}$ $-$ 31° 0.94; Py); ν_{max}^{nujol} 3460 cm^{-1}; NMR(Py): δ 4.84 (H-1′, *d*, $J_{1',2'}$ 8.0 Hz), 1.62 (2H, *q*, *J* 6 Hz, Me–CH_2–C–), 1.28 (6H, *s*, C(Me)$_2$), 0.95 (3H, *t*, –CH_2–CH_3). Found: C 53.35; H 8.86. $C_{11}H_{22}O_6$ requires: C 52.78; H 8.86).

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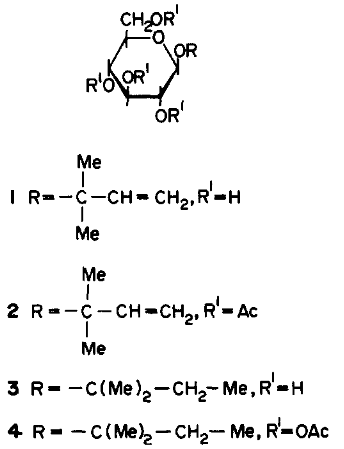
*J. Borja does not agree with J. F. M. Cannon, (1968) *Flora Europeae* Vol. 2 p. 359 (Cambridge University Press) who identifies *Ferula loscosii* with *F. communis* L., since the former considers it is a particular species. (Personal communication Dr. J. Borja, Instituto Botánico A. J. Cavanilles, Madrid).



1 R = $-C(Me)_2-CH=CH_2$, R' = H

2 R = $-C(Me)_2-CH=CH_2$, R' = Ac

3 R = $-C(Me)_2-CH_2-Me$, R' = H

4 R = $-C(Me)_2-CH_2-Me$, R' = 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′$_{1}$, *q*, $J_{6'_1 6'_2}$ 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,l 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