

# A NEW DERIVATIVE OF THE SESQUITERPENE 3-DEOXY-8-EPI-MAYTOL FROM *EUONYMUS EUROPAEUS*\*

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**Key Word Index**—*Euonymus europaeus*; Celastraceae; polyester of sesquiterpene alcohol; constitution; 3-deoxy-8-*epi*-maytol.

Seeds of *Euonymus europaeus* collected in the neighbourhood of the city of Bratislava were dried and ground. The *n*-heptane extraction removed oils and sesquiterpene alkaloids from the seeds [2-7]. Further maceration with benzene and work-up afforded a residue which was chromatographed on alumina. Rechromatography of fractions containing the mixture of esterified sesquiterpene polyols on Si gel gave, in addition to the known esters [8-10] of 7 $\beta$ -hydroxy-3,4-dideoxy-8-*epi*-maytol (A-1, 1 and A-2, 2) and esters of 3-deoxy-8-*epi*-maytol (B-1, 3 and B-4, 4), a new sesquiterpene ester B-5 (5).

Ester B-5 (amorphous), C<sub>36</sub>H<sub>50</sub>O<sub>12</sub>, M<sup>+</sup> 674, [ $\alpha$ ]<sub>D</sub><sup>24</sup> +46.8 (c 0.5, EtOH); IR (2.5 mM, CCl<sub>4</sub>),  $\nu_{\max}$  cm<sup>-1</sup>: 3570, 1150 (*tert*-OH), 2980, 1750 (COOR), 1720 (PhCOOR), 1620, 1375; MS *m/e*: M - Me (for C<sub>35</sub>H<sub>47</sub>O<sub>12</sub> calculated: 659.3067; found: 659.3070), M - C<sub>2</sub>H<sub>2</sub>O, M - C<sub>4</sub>H<sub>5</sub>COOH, M - Me - PhCOOH (*m*\* 659  $\rightarrow$  537), M - C<sub>4</sub>H<sub>9</sub>COOH - HOAc, M - C<sub>4</sub>H<sub>9</sub>COOH - HOAc - PhCOOH (*m*\* 512  $\rightarrow$  390), 202 (C<sub>13</sub>H<sub>14</sub>O<sub>2</sub>), 166 (C<sub>9</sub>H<sub>10</sub>O<sub>3</sub>), 105, 85, 77, 57, 43; <sup>1</sup>H NMR (CHCl<sub>3</sub>, 80 MHz):  $\delta$  5.74 (*d*, *J* = 3.5 Hz, H-1), 5.59 (*m*, H-2), 6.20 (*s*, H-5), 5.35 (*dd*, *J*<sub>8a,7a</sub> = 7 Hz, *J*<sub>8a,7e</sub> > 0 Hz, H-8), 5.11, 4.48 (*ABq*, *J* = 13 Hz, H-11); 1.62, 1.56, 1.54 (*s*, 3  $\times$  3H, 3 *tert*-C-Me).

From the peak ratio M - 15/M it is suggested that 5 is a derivative of 3-deoxy-8-*epi*-maytol (alcohol B) [8]; peaks at *m/e* 105 and 77 are indicative of a PhCOO-

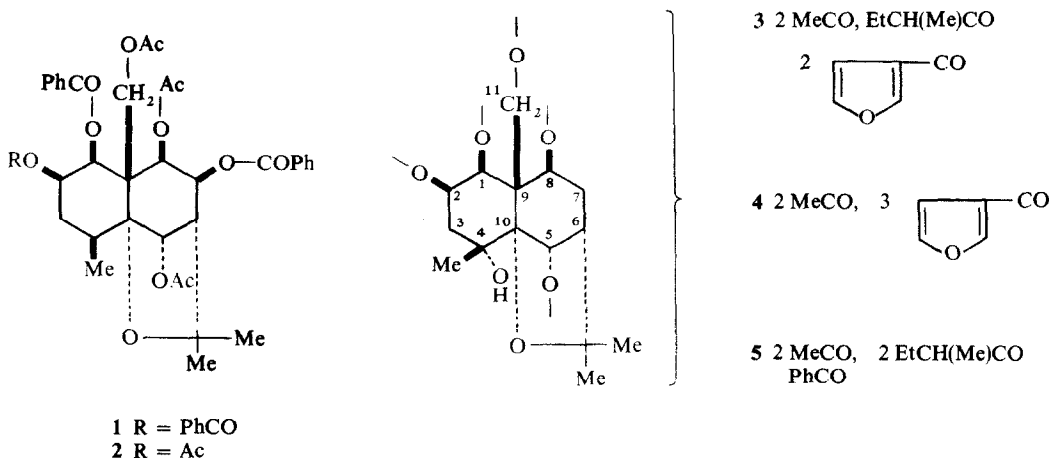
85 and 87 of C<sub>4</sub>H<sub>9</sub>COO-, and 43 of CH<sub>3</sub>COO-Me groups thus characterizing the respective acid residues. The stereochemistry at C-8 was backed by the multiplicity in the <sup>1</sup>H NMR spectrum of the proton involved. Since other positions and multiplicities of protons due to the resonance of the skeleton of 5 were also very close to those reported for the ester B-4 [8], an identical spatial arrangement is ascribed to the ester B-5. Based upon the position of the vibration band in the IR spectrum [11] and biogenetic considerations, the hydroxy group at C-4 is assigned the equatorial orientation.

The number of individual ester-bound acids was determined on the basis of the <sup>1</sup>H NMR spectrum. Signals of both acetyl groups resonated at  $\delta$  2.32 and 2.16 (*s*, 2  $\times$  3H), protons of the benzoyl group at 8.05 (2 protons adjacent to carbonyl) and 7.62-7.32 (*m*, 3H). Two doublets at 1.25 (*J* = 7 Hz) and two triplets at 0.90 were ascribed to the respective protons of  $\alpha$ -Me and terminal Me groups of two molecules of  $\alpha$ -methylbutyric acid.

On the basis of the arguments presented we propose the structural formula 5 for the ester B-5.

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## GERIN, A EUDESMANE METHYL ESTER IN TRICHOME EXUDATES OF *GERAEA VISCIDA*

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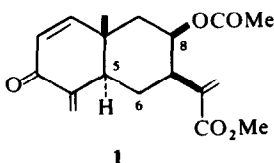
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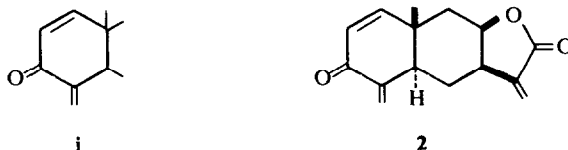
**Key Word Index**—*Geraea viscida*; Compositae; trichome exudate; gerin; sesquiterpene methyl ester.

Our continuing phytochemical investigations of California plants which are reported to exhibit cytotoxic activity and cause allergic contact dermatitis in humans, prompts us to report the structure elucidation of gerin (**1**), a sesquiterpene methyl ester from *Geraea viscida* (Gray) Blake. This naturally occurring plant constituent, present in copious amounts in the leaf trichomes, belongs to the eudesmane skeletal class of sesquiterpenes, and is similar to arbusculin-E methyl ester, a known eudesmane from *Artemisia arbuscula* var. *arbuscula* [1].



Gerin (mp 140.0–141.5°), isolated in 0.12% yield from *Geraea viscida*, had the composition  $C_{18}H_{22}O_3$  and its MS exhibited a molecular ion peak at  $m/e$  318, along with peaks at  $m/e$  275 ( $M - 43$ ), 258 ( $M - 60$ ), 247 ( $M - 75$ ), 232 ( $M - 86$ ) and a base peak at  $m/e$  43. The IR spectrum of **1** contained a very strong band (broad) at  $1727\text{ cm}^{-1}$  (ester) and sharp bands at 1670 and  $1625\text{ cm}^{-1}$ , indicative of a cross-conjugated dienone system. In addition, gerin showed ultraviolet absorption at 239 nm ( $\epsilon$  11029) indicating the presence of an  $\alpha,\beta$ -unsaturated ketone unit, and end absorption at 202 nm ( $\epsilon$  11348). The 250 MHz  $^1\text{H}$  NMR spectrum of gerin revealed a pair of sharp doublets located at  $\delta$  6.86 and 5.99 (1 proton each,  $J = 10\text{ Hz}$ ) having the characteristic AB pattern of a  $\gamma,\gamma$ -disubstituted cyclohexenone. The presence of a sharp three-proton singlet at  $\delta$  1.15 (tertiary

methyl) and a pair of signals at  $\delta$  6.15 ( $q$ ) and 5.29 ( $t$ ) lead to the conclusion that gerin possessed the partial structure **i**. The spectral characteristics were in very close agreement with the NMR, IR and UV spectra recorded for encelin (**2**), a eudesmanolide isolated from *Encelia farinosa* (Compositae) which also possesses a ring A cross-conjugated dienone system [2].



The presence of a sharp three-proton singlet at  $\delta$  1.98 and a one-proton quartet at  $\delta$  5.36 suggested the presence of an acetate. In addition, the  $^1\text{H}$  NMR spectrum revealed a pair of singlets (6.34 and 5.68, one proton each) characteristic of a methylene group conjugated with a carbonyl group. These data, coupled with a three-proton singlet located at 3.78, clearly established the presence of a methyl  $\alpha$ -substituted acrylate moiety. These observations lead to the conclusion that gerin possessed the partial structure **ii**.

