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IRIDOIDS OF *CYMBALARIA-MURALIS**

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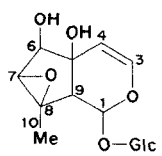
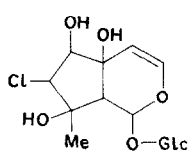
Key Word Index—*Cymbalaria muralis*; Scrophulariaceae,: iridoids; antirrhinoside; linarioside.

Plant. Cymbalaria muralis Per. *Source.* Hungary and Yugoslavia. *Uses.* Medicinal.[1] *Previous work.* Presence of glycosides.[2]

Present work. The MeOH extract of the air dried plant, when subjected to TLC showed the presence of iridoid glycosides, two of them in major amounts. Adsorption[3] on charcoal and elution with H_2O–EtOH was used for preliminary purification. The light yellow amorphous material obtained from the eluate (20% and 30% EtOH in H_2O) was subjected to partition chromatography on silica gel[4] using *t*-BuOH sat. with H_2O as eluent. Two compounds 1 and 2 were isolated in pure form.



(1)



(2)

Compound **1** (antirrhinoside): $C_{15}H_{22}O_{10}$, a white amorphous substance $[\alpha]_D^{26}$ − 79° (dioxane); λ_{max}^{MeOH} 207 nm; ν_{max}^{KBr} 3450, 1660 cm^{-1}; NMR (D_2O, TMS as external reference δ ppm) 5·50 (1H, *d*, *J* 6·5, H at C-1), 6·49 (1H, *d*, *J* 6·5, H at C-3), 5·10 (1H, *d*, *J* 6·5, H at C-4), 4·10 (1H, *d*, *J* 2, H at C-6), 3·60 (1H, *d*, *J* 2, H at C-7), 2·50 (1H, *d*, *J* 6·5, H at C-9) and 1·51 (3H, *s*, Me at C-10); Formed penta acetate $C_{25}H_{32}O_{15}$ m.p. 138–39° (from aceton–hexane) and a hexa acetate $C_{27}H_{34}O_{16}$ m.p. 174°.

Compound **2** (Linarioside). A pale yellow hygroscopic substance $[\alpha]_D^{26}$ − 148° (wet dioxane): λ_{max}^{MeOH} 210 nm; ν_{max}^{KBr} 3470, 1666 cm^{-1}. On acetylation formed a mixture of hexa and hepta acetate, which were separated on a column of silicagel. Hexaacetate: $C_{27}H_{35}O_{16}$ Cl m.p. 180°. ν_{max}^{KBr} 3450 (hydroxyl), 1760, 1725, 1240 (acetate) and 1655 cm^{-1}

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(enol ether). NMR ($CDCl_3$); 6·30 (1H, *d*, *J* 6·5, H at C-3), 5·70 (1H, *dd*, *J* 6·5 and 2, H at C-4), 5·6 (1H, *brs*, H at C-1), 3·45 (1H, *brs*, H at C-9) and 1·5 (3H, *s*, methyl at C-10). Hepta acetate: $C_{29}H_{37}O_{17}Cl$ m.p. 146–148° ν_{max}^{KBr} 1755, 1735, 1250 (acetate) and 1650 cm^{-1} (enol ether), NMR ($CDCl_3$); 6·3 (1H, *d*, *J* 6·5, H at C-3), 6·15 (1H, *s*. H at C-1), 5·65 (1H, *dd*, *J* 6·5 and 2, H at C-4), 3·65 (1H, *brs*, H at C-9) and 1·63 (3H, *s*, methyl at C-10). Identical with an authentic [5] sample of hexa and hepta linarioside acetates (TLC, IR and mixed melting point).

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DITERPENES FROM *CARYOPTERIS DIVARICATA*

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Key Word Index—*Caryopteris divaricata*; Verbenaceae; diterpenes; insect anti-feeding compounds; caryoptinol; dihydrocaryoptinol.

Previously we reported the isolation and structural elucidation of six insect antifeeding diterpenes including the principal diterpene caryoptin (**1**) from the leaves and stems of *Caryopteris divaricata* Maxim.[1] In a further survey of the minor diterpene components in this plant, we have obtained two new diterpenes, caryoptinol (**2**) and dihydrocaryoptinol (**3**). These compounds have been related to the known dihydrocaryoptin (**4**). The new compounds have a bitter taste and possess antifeeding activity against the larvae of tobacco cut worm, *Spodoptera litura* F.

Caryoptinol (**2**) (0·00004% yield from dry wt) had, m.p. 219–220°; $[\alpha]_D$ −83° (*c* 0·33, $CHCl_3$); ν_{max}(THF) 3590, 3520, (KBr) 3520, 1730, 1720, 1620, 1260, 1235 cm^{-1} (Calc. for $C_{24}H_{34}O_8$: C, 63·98; H, 7·61. Found: C, 64·23; H, 7·53%). (**2**) contained one tertiary methyl, one secondary methyl group, two acetate residues and one secondary hydroxy group. The NMR spectrum showed the AB quartet, typical of a primary carbinol group at δ5·30 and 4·45 ppm (18-H_2, *J* 11·0 Hz).

The appearance of A-proton signal at δ5·30 ppm was by 0·33 ppm lower field than that of caryoptin. Further, the NMR spectrum showed the doublet signals of the AX type (δ_2–δ_1/J ~ 42)[2] at δ2·22 and 3·03 ppm (17-H_2, *J* 4·5 Hz) due to an epoxide methylene group: a broad singlet at δ3·31 ppm (W 1/2 *ca* 6 Hz) based on an equatorial C-3 proton; and broad signal overlapping other signal at δ4·70 ppm due to an axial C-6 proton.

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