(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.

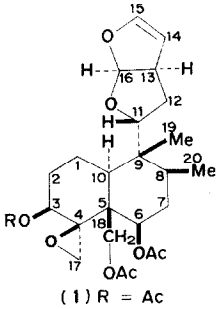
Previously we reported the isolation and structural elucidation of six insect antifeeding diterpenes including the principal diterpene caryoptin (**1**) from the leaves and stems of *Caryopteris divaricata* Maxim.[1] In a further survey of the minor diterpene components in this plant, we have obtained 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).

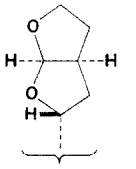
The appearance of A-proton signal at δ5·30 ppm was by 0·33 ppm lower field than that of caryoptin. Further, the NMR spectrum showed the doublet signals of the AX type (δ_2–δ_1/J ~ 42)[2] at δ2·22 and 3·03 ppm (17-H_2, *J* 4·5 Hz) due to an epoxide methylene group: a broad singlet at δ3·31 ppm (W 1/2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

[1] HOSOZAWA, S., KATO, N. and MUNAKATA, K. (1973) *Phytochemistry* **12**, 1833.
[2] SILVERSTEIN, R. M. and BASSLER, G. C. (1963) *Spectrometric Identification of Organic Compounds*, pp. 77, Wiley, New York.

The presence of a tetrahydrofurofuran ring was shown by the following data. The triplet signals showed at δ4·81 and 6·44 ppm (14- and 15-H, J 2·5 Hz). A doublet at the downfield (δ6·02 ppm, J 6·5 Hz), a double doublet at δ4·00 ppm (J 10·0, 6·5 Hz), and a broad signal centered at δ3·58 ppm (W 1/2 *ca* 15 Hz) were assigned to C-16, C-11, and C-13 protons, respectively, which were commonly observed in the furofuran ring.[1,3,4]



(1) R = Ac
(2) R = H



(3) R = H
(4) R = Ac

Catalytic reduction of (**2**) with Pd–C gave a dihydroderivative (**3**), m.p. 204–205°; $[\alpha]_D$ −73° (*c* 0·26, $CHCl_3$). In the NMR spectrum of (**3**), C-15 methylene protons appeared at δ3·81 ppm as a doublet (J 7·5 Hz) and at δ3·88 ppm as a double doublet (J 7·5, 2·2 Hz). (**3**) was identified as dihydrocaryoptinol (0·00001 % yield on dried basis) by comparison of the spectroscopic data. MS of (**2**) and (**3**) showed characteristic intense fragment peaks at *m/e* 111 and 113, respectively, attributed to the furofuran ring.

Acetylation of caryoptinol (**2**) did not occur with acetic anhydride in pyridine at room temp. and it decomposed on refluxing. On the other hand, acetylation of dihydrocaryoptinol (**3**) with acetic anhydride—pyridine under reflux gave an acetate derivative, which was identified as dihydrocaryoptin (**4**) by comparison of the spectroscopic data.

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[4] KATO, N., SHIBAYAMA, S. and MUNAKATA, K. (1971) *Chem. Commun.* 1632; (1973) *J. Chem. Soc. Perkin I* 712.