Phytochemistry, 1973, Vol. 12, pp. 1833 to 1834. Pergamon Press. Printed in England.

DITERPENOIDS FROM *CARYOPTERIS DIVARICATA*

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(*Received* 2 *January* 1973. *Accepted* 23 *January* 1973)

Key Word Index—*Caryopteris divaricata*; Verbenaceae; diterpenoids; insect antifeeding compounds, caryoptin; dihydrocaryoptin; caryoptin hemiacetal.

THE isolation and structural elucidation of caryoptin (I), dihydrocaryoptin (II) and caryoptin hemiacetal (III), three new insect antifeeding diterpenoids from *Caryopteris divaricata* Maxim, are reported. In addition, clerodin (IV), clerodin hemiacetal (V), previously isolated from *Clerodendron infortunatum*,[1–3] and dihydroclerodin-I (VI) were also isolated. Dihydroclerodin-I appeared to be the first reported natural product in this plant. The new compounds were shown to be (I), (II) and (III) having the same skeleton as clerodin (IV). It is interesting that compounds containing this clerodon skeleton are found both in *Clerodendron*[4] and in *Caryopteris* species. These compounds have a bitter taste and possess an antifeeding activity against the larvae of *Spodoptera litura* F.

Ether extracts of the air-dried ground leaves and stalks of *Caryopteris divaricata* gave six compounds by column chromatography on alumina (Brockmann grade IV) and silica gel. All these compounds were shown to be closely related chemically from spectroscopic data. Caryoptin (I) (0·01 % yield on air-dried basis) had, m.p. 176–7°; $[\alpha]_D$ −91° (*c* 1·10, $CHCl_3$) and ν_{max} (KBr) 1745 sh, 1735, 1720, 1615, 1245, 1215 cm^{-1}. (Calcd. for $C_{26}H_{36}O_9$: C, 63·40; H, 7·37. Found C, 63·68; H, 7·57 %)

(I) contained one tertiary methyl, one secondary methyl group and three acetate residues. The NMR spectrum showed the two *AB* quartets, typical of a primary carbinol methylene group at δ 4·97 and 4·50 ppm (18-H_2, *J* 13·0 Hz), two from an epoxide methylene group at δ 3·08 and 2·28 ppm (17-H_2, *J* 4·5 Hz); a broad double doublet centered at δ 4·70 ppm due to an axial C-6 proton; and a broad singlet at δ 4·50 ppm based on an equatorial C-3 proton. The presence of a tetrahydro-furofuran ring was shown by the following data. The triplet signals characteristic of the dihydrofuran ring showed at δ 4·80 and 6·46 ppm (14- and 15-H, *J* 2·5 Hz). A doublet at the downfield (δ 5·99 ppm, *J* 6·2 Hz) and a doule doublet at δ 4·01 ppm (*J* 9·0 and 7·5 Hz) were assigned to C-16 and C-11 protons, respectively, commonly observed with furofuran rings.[2,4]

Catalytic reduction of (I) with Pd–C gave a dihydroderivative (II), m.p. 198·5–199·5°; $[\alpha]_D$ −63° (*c* 1·13, $CHCl_3$). In the NMR spectrum of (II), C-15 methylene protons appeared at δ 3·81 ppm as a doublet (*J* 7·5 Hz) and at δ 3·88 ppm as a double doublet (*J* 7·5 and 2·2 Hz). This dihydro-derivative was identified as dihydrocaryoptin (II), one of the minor components isolated, by comparison of spectroscopic data and the specific rotation.

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Caryoptin hemiacetal (III) was isolated from the more polar fractions on alumina column chromatography. The compound, crystallized from ethyl acetate–light petrol., gave colorless prisms, m.p. 188–189° (Calcd. for $C_{26}H_{38}O_{10}$; C, 61·16; H, 7·50. Found C, 61·22; H, 7·58%). Treatment of (III) with manganese dioxide smoothly gave a γ-lactone derivative (VII), m.p. 117–118°; $[\alpha]_D$ $-64°$ (c 0·34, $CHCl_3$) with IR absorption at 1780 cm^{-1} (γ-lactone) and disappearance of the epimeric proton signals at C-15 in the NMR spectrum. Mass spectra of (I), (II) and (VII) showed characteristic intense fragment peaks at *m/e* 111, 113 and 127, respectively, attributed to the furofuran ring.

The position and configuration of the 3β-acetoxyl group was revealed from analysis of the NMR spectra and further confirmed by the following studies. A dihydrotetraol derivative (IX) obtained by reduction of (II) with $LiAlH_4$ rapidly consumed one equivalent of HIO_4. It was found that C-3—C-4 bond fission had occurred in (IX), since the resulting keto-aldehyde derivative (X) exhibited carbonyl absorptions at ν_{max} ($CHCl_3$) 1700 and 1720 cm^{-1} and aldehydic proton and methyl ketone signals at δ 9·75 and 2·40 ppm, respectively. When (IX) was treated with 2,2-dimethoxy propane and *p*-toluene sulfonic acid, it formed a diacetonide derivative (XI). This will be described elsewhere.

A second major crystalline compound from *C. divaricata* (IV), m.p. 164–165° was, identified as clerodin by comparison with an authentic sample using spectroscopic data, m.p. and specific rotation. Catalytic hydrogenation of (IV) gave another isolated compound dihydroclerodin-I,[2] which was identical with the natural product (VI). The final isolated compound (V), m.p. 179–181°, was an epimeric mixture at C-15. Oxidation of (V) under similar condition as (III) afforded a γ-lactone derivative (VIII), which gave the same NMR and IR spectra data as clerodin γ-lactone, m.p. 191–192°; $[\alpha]_D$ $-25°$ (c 0·75, $CHCl_3$).

Acknowledgement—An authentic sample of clerodin was kindly provided by Professor D. H. R. Barton.