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DITERPENOIDS FROM *CLERODENDRON CALAMITOSUM*

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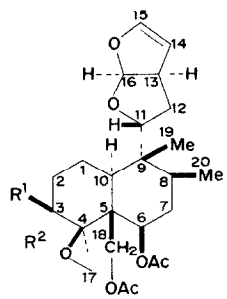
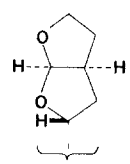
Key Word Index—*Clerodendron calamitosum* Verbenaceae, diterpenoid 3-epicaryoptin antifeeding compound

Previously we reported the isolation and structural elucidation of six insect antifeeding diterpenoids including the principal diterpenoid caryoptin (**1**) from the ground leaves and stems of *Caryopteris divaricata* Maxim [1] In further scrutiny of diterpenoids having the same skeleton as clerodin (**2**)[1-4] in plants of the Verbenaceae, we have obtained a new diterpenoid 3-epicaryoptin (**3**) from *Clerodendron calamitosum* L It is interesting in view of biogenesis that caryoptin is not found but 3-epicaryoptin is observed in this plant This new compound has a bitter taste and possesses antifeeding activity against the larvae of *Spodoptera litura* F

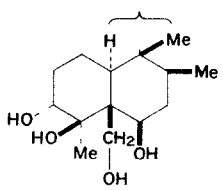
Ether extracts of the air dried leaves of *Clerodendron calamitosum* gave an antifeeding compound as main component by column chromatography on alumina (Brockmann grade V gradient elution with Et_2O–C_6H_6) and silica gel This compound and caryoptin were shown to be closely related chemically from spectroscopic data 3-Epicaryoptin (**3**) (0·01% yield on air dried bases) had, m p 171–172 °, $[\alpha]_D$ − 70 (*c* 1·01, $CHCl_3$) and ν_{max} (KBr) 1735, 1620 1250, 1240 cm^{-1} (Calcd for $C_{26}H_{36}O_9$ C 63·40, H 7·37 Found C, 63·51, H, 7·31%)



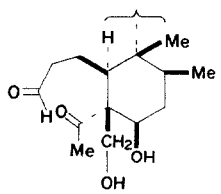
(**1**) R^1 = OAc, R^2 = H
(**2**) R^1 = R^2 = H
(**3**) R^1 = H, R^2 = OAc



(**4**) R^1 = H, R^2 = OAc
(**7**) R^1 = OAc, R^2 = H



(**5**)



(**6**)

(**3**) contained one tertiary methyl, one secondary methyl group and three acetate residues The NMR spectrum showed the two AB quartets, a primary carbinol methylene

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[2] SIM G A HAMOR T A PAUL I C and MONTEATH ROBERTSON I (1961) *Proc Chem Soc* 75
[3] BARTON D H R CHEUNG N T CROSS A D JACKMAN L M and MARTIN SMITH M (1961) *Proc Chem Soc* 76 (1961) *J Chem Soc* 5061
[4] PAUL I C SIM G A HAMOR T A and MONTEATH ROBERTSON I (1962) *J Chem Soc* 4133

group at δ 4 79 and 4 38 ppm (18-H_2, J 12 5 Hz), and an epoxide methylene group at δ 2 84 and 2 59 ppm (17-H_2, J 4 5), a double doublet at δ 5 30 ppm (J 12 0, 5 0) due to an axial C-3 proton, and a broad signal overlapping other absorption at δ 4 65–4 85 ppm based on an axial C-6 proton The presence of a tetrahydrofurofuran ring was shown by the following data The triplet signals characteristic of the dihydrofuran ring showed δ 4 81 and 6 49 ppm (14- and 15-H, J 2 0) A doublet at the down-field (δ 6 02 ppm, J 6 5 Hz), a double doublet at δ 4 02 ppm (J 10 0, 6 5 Hz), and a broad signal centered at δ 3 59 ppm (W 1/2 *ca* 15 Hz) were assigned to C-16, C-11 and C-13 protons, respectively, commonly observed in the compounds containing furofuran rings [1,3,5]

Catalytic reduction of (**3**) with Pd–C(10%) gave a dihydroderivative (**4**), m p 161–162°, $[\alpha]_D$ −42° (*c* 1 04, $CHCl_3$) In the NMR spectrum of (**4**), C-15 methylene protons appeared at δ 3 85 ppm as a doublet (J 7 5 Hz) and at δ 3 92 ppm as a broad doublet (J 7 5 Hz) MS of (**3**) and (**4**) showed characteristic intense fragment peaks at *m/e* 111 and 113, respectively, attributed to the furofuran ring

The position and configuration of the 3α-acetoxyl group was revealed from analysis of the NMR spectra and further confirmed by the following studies A dihydrotetraol derivative (**5**) obtained by reduction of (**4**) with $LiAlH_4$ slowly consumed one equivalent of $NaIO_4$ in MeOH–H_2O It was found that C-3–C-4 bond fission had occurred in (**5**), since the resulting keto-aldehyde derivative (**6**) exhibited carbonyl absorption 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 (**6**) was identified as keto-aldehyde derivative[1] derived from dihydrocaryoptin (**7**) by comparison with authentic sample using spectroscopic data and specific rotation, $[\alpha]_D$ +18° (*c* 0 34, $CHCl_3$)

In addition, the optical rotation of the compounds having tetrahydro furofuran ring paralleled the rotations of compounds containing dihydrofuran ring In the clerodin series, clerodin had $[\alpha]_D$ −53°, 3-epicaryoptin had $[\alpha]_D$ −70°, caryoptin had $[\alpha]_D$ −91°, dihydro derivative series, dihydroclerodin-I had $[\alpha]_D$ −17°, 3-epidihydrocaryoptin had $[\alpha]_D$ −42°, dihydrocaryoptin had $[\alpha]_D$ −63° These experimental data supported that the absolute configuration of 3-epicaryoptin may be the same as that of clerodin except at C-3 position

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[5] KATO, N, SHIBAYAMA, S and MUNAKATA, K (1971) *Chem Commun* 1632, (1973) *J C S Perkin I*, 712