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EUDESMANE DERIVATIVES FROM *EPALTES DIVERICATA**

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Key Word Index—*Epaltes divericata*; Compositae; sesquiterpenoids; eudesmane derivative.

Abstract—Five closely related eudesmane derivatives have been isolated from the acetone extract of *Epaltes divericata*. A new eudesmane natural product has been isolated and its structure established by chemical correlation and spectral data as 3α-angeloyloxy-4α-acetoxy-8-oxoeudesm-7(10)-ene.

In the course of our work on the chemistry of the Compositae, we have isolated five closely related sesquiterpenoids (**1**, **2**, **5**–**7**) possessing the eudesmane skeleton from the acetone extract of *Epaltes divericata* Cass (family Compositae, tribe Inulae). Of these five sesquiterpenoids the structure of the only new compound (**2**), which differs from the known derivative of cuauhtemone by the nature of the side chain, was established as 3α-angeloyloxy-4α-acetoxy-8-oxo-eudesm-7(10)-ene by comparison of its spectral properties and correlation with cuauhtemone (**4**) [1].

Compound **2**, $C_{22}H_{32}O_5$, *m/z* 376 ([M]$^+$, 2%), obtained as a liquid, exhibited in its ^{1}H NMR spectrum the same spectral features as the derivatives of cuauhtemone [1] except for the nature of the side chain. Thus, instead of an epoxyangeloyl group, the ^{1}H NMR spectrum showed the characteristic signals of an angeloyl group at δ6.15 (*qq*). This was further confirmed by its hydrolysis to give **4**, whose structure has been unequivocally proved by X-ray crystallography [2].

The structure of another constituent (**1**), previously isolated from *Pluchea suaveolens* [3], has been proposed as the C-3 epimer of compound **2** mainly on the basis of its ^{1}H NMR spectral data. In fact, the ^{1}H NMR spectral features of compound **1** were the same as those of **2** except for the H-3 signal.

However, in view of the presence of more than one asymmetric centre, unequivocal proof for the structure of **1** was sought by X-ray crystallography and a close comparison of the torsion angles of **1** and **4** (Table 1) confirmed the structure of **1**.

Crystal data. $C_{22}H_{32}O_5$. A crystal of approximate size 0.37 × 0.55 × 0.65 mm was used. Data collection was done on an Enraf Nonius CAD4F-11M single-crystal X-ray diffractometer using $\omega/2\theta$ scan mode with $\theta < 23.5$ ($\lambda = 0.7107$ Å). The crystals belong to the tetragonal space group $P4_3$, with $a = b = 7.815$ (1) Å, $c = 34.649(6)$ Å and $Z = 4$. The structure was solved using the MULTAN-78 program [4].

The current R is 0.180. The acetate and angeloyl are *trans* with respect to each other. Several interesting features of the stereochemical details will appear elsewhere after completion of the refinement.

The isolation of closely related eudesmane derivatives from *E. divericata* lends further support for the relationship of *Epaltes* [5], *Pluchea* [6, 7] and *Blumea* species [8].

EXPERIMENTAL

Mps were determined in a Kofler apparatus and are uncorr. Optical rotations were taken for solns in MeOH. ^{13}C NMR and ^{1}H NMR spectra for solns in $CDCl_3$ with TMS as internal standard. Mass spectra were determined at 70 eV using a direct inlet system.

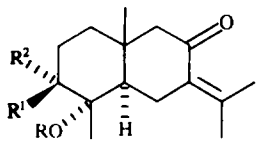
The whole plant of *E. divericata*, collected during November 1982 near Goa (India), was shade-dried, powdered and the powder (2 kg) extracted with Me_2CO. The Me_2CO extract (70 g), obtained as a thick viscous oil, was fractionated on a silica gel column into four broad fractions: A, B, C and D.

Compound **1**. Fraction B on repeated preparative TLC gave a colourless crystalline compound (150 mg), mp 75–76° (petrol–Et$_2$O) (lit. [3] gum), $[\alpha]_D + 51.51°$ ($CHCl_3$). ^{13}C NMR: δ33.404 *t* (C-1), 23.071 *t* (C-2), 72.334 *d* (C-3), 83.447 *s* (C-4), 45.558 *d* (C-5), 26.061 *t* (C-6), 130.500 *s* (C-7), 210.729 *s* (C-8), 60.404 *t* (C-9), 36.004 *s* (C-10), 146.097 *s* (C-11), 23.74 *q* (C-12), 23.071 *q* (C-13), 19.302 *q* (C-14), 18.327 *q* (C-15), 169.624 (acetoxy carbonyl), 22.001 *q* (acetoxy methyl), OAng: 166.504 *s*, 22.861 *q*, 128.225 *s*, 130.104 *d*, 15.857 *q*.

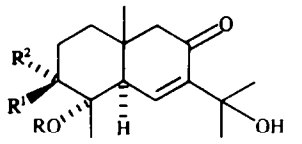
Table 1. Comparison of torsion angles (in degrees) of compounds **1** and **4**

	1	**4**
C(1)–C(2)–C(3)–O(16)	175.6	−65
C(2)–C(3)–C(4)–O(17)	−174	−169
C(2)–C(3)–C(4)–C(14)	83.8	78
C(14)–C(4)–C(3)–O(16)	−40.6	−160
O(17)–C(4)–C(3)–O(16)	61.1	−45.9
C(15)–C(10)–C(1)–C(2)	−70	−73
C(6)–C(5)–C(4)–C(14)	62	56
C(6)–C(5)–C(4)–O(17)	−41	−62

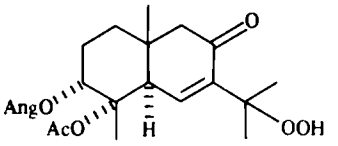
*N.C.L. Communication No. 3975.



1 R = Ac; R^1 = OAng; R^2 = H
2 R = Ac; R^1 = H; R^2 = OAng
3 R = H; R^1 = OH; R^2 = H
4 R = H; R^1 = H; R^2 = OH



5 R = Ac; R^1 = OAng; R^2 = H
6 R = Ac; R^1 = H; R^2 = OAng



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Compound **2**. Fraction B gave a liquid (200 mg) on repeated preparative TLC, $[\alpha]_D$ + 139.20°; UV λ_{max}^{MeOH} nm (ε): 219 (31 950), 255 (21 950); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1735, 1715, 1675, 1240; ^1H NMR (90 MHz): δ5.92 *dd* (1H, *J* = 3.5, 2 Hz, H-3), 2.88 *dd* (1H, *J* = 13, 4 Hz, H-6), 2.26 *s* (2H, H-9), 2.02 *d* (3H, *J* = 2 Hz, H-12), 1.88 *s* (3H, H-13), 1.64 *s* (3H, H-14), 0.98 *s* (3H, H-15), OAng: 1.94 *dq* (3H, *J* = 1.5 Hz), 1.91 *dq* (3H, *J* = 1.5 Hz), 6.15 *qq* (1H, *J* = 7 Hz), 1.96 *s* (3H, acetoxy methyl). ^{13}C NMR: δ37.954 *t* (C-1), 25.996 *t* (C-2), 74.218 *d* (C-3), 87.671 *s* (C-4), 45.103 *d* (C-5), 25.801 *t* (C-6), 130.240 *s* (C-7), 202.119 *s* (C-8), 60.180 *t* (C-9), 37.109 *s* (C-10), 144.668 *s* (C-11), 23.461 *q* (C-12), 22.876 *q* (C-13), 19.562 *q* (C-14), 16.897 *q* (C-15), 170.664 *s* (acetoxy carbonyl), 22.681 *q* (acetoxy methyl), OAng: 167.284 *s*, 20.796 *q*, 128.355 *s*, 137.974 *d*, 15.857 *q*; *m/z* (rel. int.): 376 $[M]^+$ (2), 316 (33), 233 (27), 216 (100), 201 (82), 83 (73).

Fraction C was repeatedly rechromatographed to yield the known compounds **5**, **6** and **7**, identified by comparing the physical constants and spectral data with those of the reported compounds.

Hydrolysis of compound **2**. Compound **2** (25 mg) in 2 ml MeOH was heated with 0.25 ml $NaHCO_3$ (5% aq. soln) at 100° for 3 hr and usual work-up gave compound **4**, 4 mg, as crystals, mp 141–143° (lit. [3] 140°); $[\alpha]_D$ + 64.85°, identified by comparison of the data with those of the reported compound.

Hydrolysis of compound **1**. Compound **1** (25 mg) was hydrolysed as described above to give compound **3**, 3 mg, as crystals, mp 68–70° (lit. [4] 68–69°); $[\alpha]_D$ + 13.30° ($CHCl_3$), identified by comparison of the data with those of the reported compound.

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