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DUKUNOLIDE D, E AND F: NEW TETRANORTRITERPENOIDS FROM THE SEEDS OF *LANSIUM DOMESTICUM*

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Key Word Index—*Lansium domesticum*; Meliaceae; seeds; dukunolides D, E, and F; X-ray analysis.

Abstract—Three new tetranortriterpenoids, named dukunolides D, E, and F, were isolated from seeds of *Lansium domesticum*, and the structures established on the basis of spectral analysis and an X-ray diffraction study.

INTRODUCTION

We have previously described the structures of dukunolides A, B, and C (**1**, **2** and **3**, respectively) isolated from seeds of a Meliaceous plant, *Lansium domesticum* [1, 2]. Three more minor constituents, named dukunolider D, E, and F have been isolated. We describe here the structure determination of these new tetranortriterpenoids (**4**, **5** and **6**) on the basis of spectral and X-ray diffraction studies.

RESULTS AND DISCUSSION

Dukunolide D (**4**), $C_{26}H_{28}O_8$, $[\alpha]_D^{14.5}$ +175.3° ($CHCl_3$; *c* 0.57); was isolated in 0.008% yield from dried seeds of *L. domesticum* as colourless crystals (mp 295.5–298). The IR spectrum (3400, 1765, 1720, 1620, 940 cm^{-1}) and UV spectrum (λ_{max} 286 nm) were similar with those of dukunolide A (**1**) or C (**3**) suggesting the presence of an $\alpha,\beta,\gamma,\delta$-unsaturated δ-lactone ring system. When the ^1H NMR spectrum of **4** was compared with that of **1**, a sharp singlet at δ3.81 due to H-6 of **1** was missing in the spectrum of **4**, and a typical ABX pattern was observed at 2.83 (*d*, *J* = 17.8 Hz), 2.96 (*d*, *J* = 8.4 Hz), and 3.33 (*dd*, *J* = 17.8 and 8.4 Hz) due to H-6, H-6′ and H-5, respectively. These data suggested the structure of dukunolide D (**4**) is 5,6-deoxydukunolide A. The ^{13}C NMR spectrum supported this assignment. Instead of the oxirane carbon signals at δ57.9 (*d*, C-6) and 72.5 (*s*, C-5) of **1**, a triplet at 31.9 (C-6) and a doublet at 48.2 (C-5) were detected.

Dukunolide E (**5**), $C_{26}H_{28}O_9$, $[\alpha]_D^{13}$ +189° ($CHCl_3$; *c*0.68), was obtained in 0.004% yield as colourless crystals (mp 270–272°). The IR (3500, 3300, 1770, 1725, 1675, 1620, 1580, 950 cm^{-1}) and UV (λ_{max} 245 nm) spectra of **5** were quite similar with those of dukunolide B (**2**) suggesting the presence of an 8,9-epoxy and an α,β-unsaturated δ-lactone ring system. In the ^1H NMR spectrum of **5**, an ABX pattern at 2.73 (*dd*, *J* = 10.1, 3.7 Hz), 2.74 (*dd*, *J* = 19.3, 3.7 Hz), and 2.97 (*dd*, *J* = 19.3, 10.1 Hz) due to H-6 and H-5 were observed instead of a sharp singlet at 3.90 due to the H-6 oxirane proton of **2**. Instead of the 5,6-oxirane carbon signal at 58.4*d* and 73.2*s* of **2**, a triplet at 33.3 and a doublet at 49.4 were detected in the ^{13}C NMR spectrum of **5**. Thus the structure of dukunolide E (**5**) was determined to be 5,6-deoxydukunolide B.

Dukunolide F (**6**), $[\alpha]_D^{14}$ +167° ($CHCl_3$; *c* 0.73), mp 268–269, was isolated in 0.017% yield, and afforded the same moleculer formula $C_{26}H_{28}O_9$ with dukunolide E (**5**). The spectral patterns (IR, UV, ^1H and ^{13}C NMR) were similar with those of **5** and dukunolide B (**2**), and suggested that the structure of **6** should be a stereoisomer of **5**. Finally the single crystal X-ray diffraction study elucidated the structure **6** (Fig. 1). The absolute configuration of this molecule was determined on the basis of the *R* configuration at C-13 and C-17 of dukunolide C *p*-

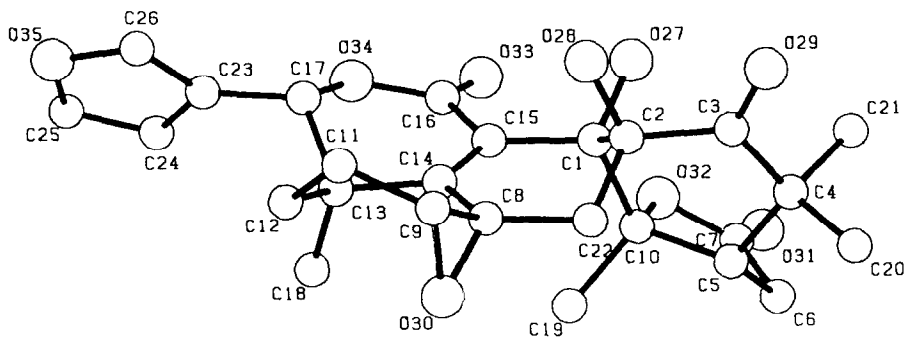

Fig. 1. ORTEP drawing of dukunolide F (**6**).

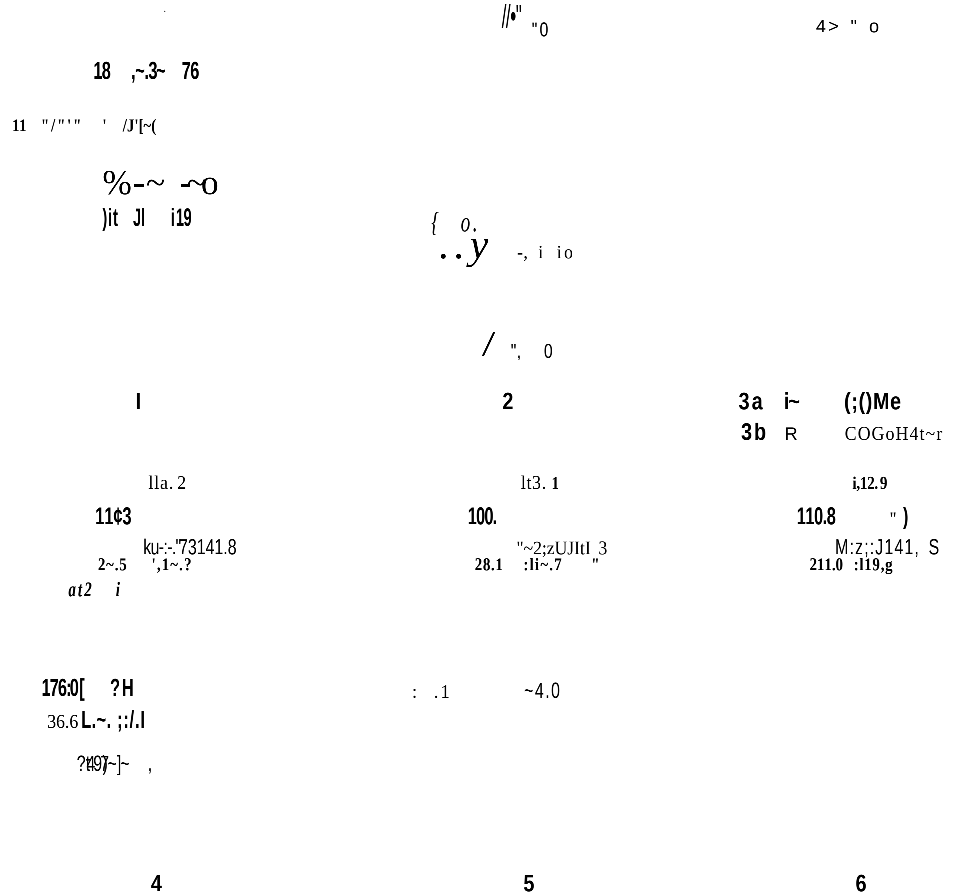

Chart 1. 4 6: 13C NMR chemical shill values 6 (4 in CsDsN, 5 and 6 in CDCI~ . *Assignments may have h) be interchanged.

bromobenzoate. [2] The hydroxyl groups at C-1 and C-2 occupy' the fl-orientation in contrast with flmse of dukunolide **A-E.**

EXPERIMENTAl,

Isolation oJ'dukunolide D 14), E (5), and F (6). Repeated silica gel CC of the CH2C12 extract of seeds of *L. domesticum* using Ctt:C12 Et20 or hexane EtOAc as eluents afforded dukunolide D (4) II00mg, 0.008'!,, yieM based on the dried seeds) as colourless crystals: mp 295.5 298' Irecyrstailized fi-om EtOAc and hexanel: [~]~)a 5 + 175.3 {CHCI~; c 0.5%: IR ,CHCI, 3400, 1765, 17217), 1620, 9411; MeOU rim; 286 (~:44701; ~HNMR (CsDsN): D1.02 (3H, s, 20), i t5 41H, *dd*+ d = 11.5, **2.2** Hz, 12~1, 1.25 (3H, s, 18), 1.39 [1H, *dd, d* :- ~i.5, 6.6 Hz, 12//I, t.44 (3H, s, 21}, !.50 (3H, s, 19), 2.12 {2H, m, 11), 2.64 (IH, d, a =- 14.4 Hz, 22fl), 2.83 (IH, d, 3 = 17.8 Hz, 6!, 2.96 (1H, d, a = 8.4 Hz, 6), 2.99 (1H, d, a=: 14.4 ttz, 22:0, 3.33 I1H, *dd, d* = 17.8, 8.4 ffz, 5}5.23 (Ill, s, *17),6.1511H, br, 9), 6.57 (lH, s, 24),* 7.61 (1H, s, 25), 7.69 (l1t, s, 26); high resolution mass *m/z* 450.1678 [M] ~, calcd for (J26H2sOs 450.1678: dukunolide E (51 (50 mg, 0.0(M ',~,yield) as colourless crystals: mp 27g 272 : [:~][)3 + 189 **(CHCI3; c 0.68): DR** KBr cm ~: 3540, 33011, 177l. 172<;~ 1675, 1620, 1580, 950; I V) i~'l°H nm" 245 I* 5269i: *H N M R iCDCI 0:6(/.98 (1H, *ddd,* J = 13.0, 4.6, 2.2 Hz, 12~k t. I2 (3H, s, *20),* 1~21 131-t,~, **18},I37{3H, s, 21i, l.60(3H,~.19),I.69tIH ~d,J - 13.2,5.1** Hz, l2fl), 1.95 {1tt, *td, J* =. 13.2, 4.6 Ilz, t 1:0, 2.10 [1H, *ddd, d = 13.2,* 5.1.2.2Hz, lIft),2.16(lH, d,J : 15.4Hz, 22~),233(IH, dd, J -- 15.4. 2.2 Hz, 22fi), 2.73 tI|L *dd, d* ~- t0. t, 3,7 Hz, 61, 2.74 (IH, *dd,* J = 19.3, L7 Hz, 61, 2.97 !Ill, *dd,* I = 19.3, 10.1 Hz, 5L 3,39 (IH, d. ,I = 2.2 Hz. 9), 3.64 (Oft), 532 {IH, ~, 171, 6.42 (IH, t, J .... L5 Hz, 24}, 7.44(1H,g,J 1.5 Hz, 25), 7.50(lft. r,J ::- 1.5 Hz, 26); high resolution mass. *m,z* 466.1632, calcd for C2~,H2~()<~ 466.1628: and dukunolide F iOi 208rag 10.0t7:,, yield) as colourlesscrystals: mp 268 269:: [~]i¢ + 167 (CHCI~;c0.731: IR ,'ctt(: .... ~: ~,350, I770. ~7?~ 680 1640.940: UV,S.nk~ta~Hran: 238 (~:4620): ~H NM R (CI)Ci~): (';i. 7 (3H, ~, 20L 121 (.31t, ~,] 8i, 130 (3H. s. 21) 1.5ii *C'-1-Lm, i2L* i 5.4 (3H, ., i9L i.84 {Itt. *d, ,1 -: 14,gHz, 22},2.03t2H, m. !tL2.a3{[H.d.J* =: 149Hz, 22j, 2.59 (IH, d,d ..... *178Hz. OL2.68iltl, d.J 8.5Hz,6),2.97(tH, dd, a* -~ 178, 8.5Hz, 5), ~,52 (111, t, ,/ 2.51tz. '#I, 376 (OH), 5.07 {OH), 5.24 !IH s, 171,6.43 {1H, ~,24). 7.42 (Ift, r, J : 1.5 ftz. 25}. 7.47 llH, s, 26L high rcsolulion mass m z 466 1039 l-M]', calcd lk:,r(22~HesOs 466. t628. lAnai catcd lot (':.}t:~(),~, C, 6445 ',, 1-t, 5.83 o, Found, C, 6437 {,,, H, 5.86 %).

Crvstal data olduk umflide t {61.(:'r*horhom bic, space group p 212,2,, a = 10.7(M 111, b -- 31.26713L c = 0.754 {11 A. Z - 4. "l'hree-dimensional intensity data v,e~e collected tm a Rigaku *AFC-5* diffractometer with graphitc-monochromated CuK:~ radiation{2 : i.54178A)usingacostalofdimenbions(l,3x0.3 × 0.1 mm 2282 Reflections ol *2422* unique ones measured m the range 0 " 70 were observed [i/'oj > *2a(Fo)].* lhe structure '*'as sobed by the direct method ,rod relined by the block-diagonal

least-squares technique to an R value of 0.035 for 2253 reflections with $|\Delta F| < 4\sigma$ (Fo). Atomic coordinates have been deposited at Cambridge Crystallographic Data Centre. The bond length between C-1 and C-10, 1.587 (4) Å, is significantly longer than the normal value expected for C (sp^3)–C(sp^3). The corresponding bond lengths of dukunolide A (1) and dukunolide C *p*-bromobenzoate (**3b**) are 1.533 Å. None of the other bond lengths are unusual. The hydroxy group at C-1 forms intramolecular hydrogen bonds with O–32 [2.574 (3) Å] and O–33 [2.722 (3) Å], and that at C-2 forms an intramolecular hydrogen bond with O–30 [2.929 (3) Å].

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