Structure of Dukunolide A: A Tetranortriterpenoid with a New Carbon Skeleton from *Lansium domesticum*

Mugio Nishizawa,*[a] Yayoi Nademoto,[a] Setijati Sastrapradja,[b] Motoo Shiro,[c] and Yuji Hayashi[a]

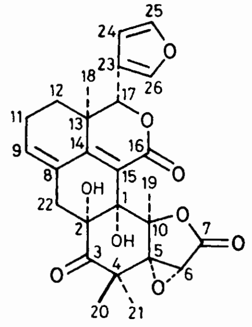
[a] *Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshiku, Osaka 558, Japan*
[b] *The National Biological Institute, Bogor, Indonesia*
[c] *Shionogi Research Laboratories, Shionogi & Co. Ltd., Fukushimaku, Osaka 553, Japan*

A tetranortriterpene, dukunolide A, having a novel skeleton, has been isolated as a bitter principle of the seeds of *Lansium domesticum*, and the structure has been established by *X*-ray analysis.

A Meliaceous plant *Lansium domesticum* Jack v. Duku[1,2] produces tasty fruits with bitter seed. From the seed extract, one of the bitter principles has been isolated as crystals, and the structure has been established by a single crystal *X*-ray diffraction analysis. The bitter principle, named dukunolide A, has a novel skeleton with 26 carbon atoms, which is a new member of the rearranged tetranortriterpenoids.[3,4]

Dukunolide A (**1**) {m.p. 279—281 °C, $[\alpha]_D^{20}$ +166° (*c* 0.9, $CHCl_3$)} was isolated in 0.03% yield as colourless needles by column chromatography, followed by recrystallization, of the hexane extract of powdered seeds of *Lansium domesticum*. The molecular formula $C_{26}H_{26}O_9$ was determined on the basis of the mass spectrum (m/z 482 for M^+) and elemental analysis. The i.r. spectrum showed the presence of hydroxy groups (3550 and 3300 cm^{-1}), carbonyls (1790, 1735, and 1670 cm^{-1}), and double bonds (1625, 1582, 1500, and 960 cm^{-1}). The existence of an α,β,γ,δ-unsaturated carbonyl moiety was suggested by the u.v. absorption spectrum ($\lambda_{max.}$ 292 nm, ε 14600). The ^1H n.m.r. spectrum was rather simple,† and the ^{13}C n.m.r. spectrum in $CDCl_3$ showed the presence of four methyls (δ 15.5, 20.4, 22.2, and 23.6), three methylenes (δ 22.2, 30.2, and 34.0) and six methines (δ 57.9, 80.3, 109.9, 140.1, 141.5, and 143.2). The existence of thirteen quaternary carbons (δ 37.9, 43.1, 72.5, 77.3, 78.1, 87.7, 113.0, 119.2, 125.3, 156.0, 167.4, 169.1, and 210.4) made the structural study very difficult by conventional spectral analysis.

The correct structure was established by a single crystal *X*-ray diffraction study. *Crystal data* for (**1**): M = 482.5, orthorhombic, space group $P2_12_12_1$, a = 12.404(1), b = 21.483(2), c = 8.747(1) Å, U = 2331.0(3) Å^3, Z = 4, D_c = 1.37 g/cm^3. The structure was solved by direct methods and refined by a block-diagonal least-squares technique to R = 0.056 for 1949 reflections [$|F_c| \geq \sigma_1(F_o)$, $|\Delta F_o| < 3\sigma_1(F_o)$, $\sigma_1(F_o) = \{\sigma^2(F_o) + 0.00205\,|F_o|^2\}^{1/2}$] of 2278 unique ones collected on a Rigaku AFC-5UD diffractometer with θ<65° for Cu-K_α radiation.‡



(**1**)

The relative configuration of the molecule is shown in Figure 1. The ring junctions at the C(1)–C(2) and C(5)–C(10) bonds are *cis*. The γ-lactone ring and the mean plane of C(1)–C(2)–C(22)–C(8)–C(14)–C(15) face each other with a dihedral angle of 43°, and the distance between C(15) and O(32) is only 2.7 Å, and that between C(7) and C(8) is 3.6 Å.

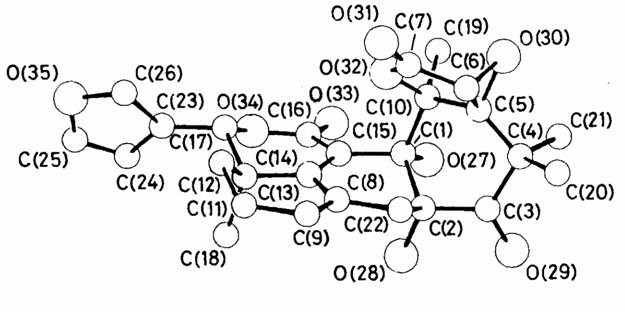
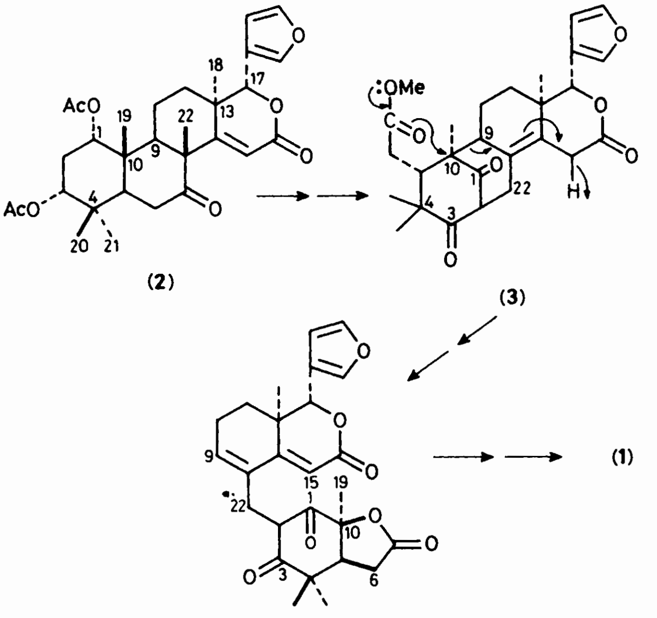


Figure 1. Computer-generated perspective drawing of dukunolide A.



(**2**)

(**3**)

(**4**)

---

† δ 1.08, 1.10, 1.48, 1.73, 2.30, 2.58, 3.51, 3.80, 5.28, 6.22, 6.45, 7.44, 7.51, and 7.87.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The existence of charge-transfer interaction is considered between the C(7) carbonyl group and the $\Delta^{8,9}$ double bond, which would explain the bathochromic shifted u.v. absorption maximum ($\lambda_{max.}$ 292 nm). The hydroxy groups form the intramolecular hydrogen bonds between O(27) and O(33), and O(28) and O(29). No unusual bond lengths and angles are found.

The biogenesis of dukunolide A could be recognized by considering the intermediary mexicanolide (**3**) or its analogues, which are derived from khivorin (**2**).[3,4,5] Fragmentation of the C(9)–C(10) bond of (**3**) accompanied by the γ-lactone formation and double bond migration would give the intermediate (**4**), which recyclizes at C(1) and C(15) to give the carbon skeleton of dukunolide A. The occurrence of (**4**) in nature has not yet been recorded.[6]

The authors thank Mr. Y. Kawakami and Mr. K. Ashizawa of Eisai Co. Ltd. for the 400 MHz n.m.r. spectra. This study was supported by a Grant-in-Aid for Special Project Research from the Ministry of Education, Science and Culture of the Japanese Government.

Received, 20th November 1984; Com. 1638

References

1 M. Nishizawa, H. Nishide, Y. Hayashi, and S. Kosela, *Tetrahedron Lett.*, 1982, **23**, 1349.

2 M. Nishizawa, H. Nishide, S. Kosela, and Y. Hayashi, *J. Org. Chem.*, 1983, **48**, 4462.

3 D. L. Dreyer, *Prog. Chem. Org. Nat. Prod.*, 1968, **26**, 190.

4 D. A. H. Taylor, *Prog. Chem. Org. Nat. Prod.*, 1984, **45**, 1.

5 S. A. Adeoye and D. A. Bekoe, *Chem. Commun.*, 1965, 301; J. D. Connolly, I. M. S. Thornton, and D. A. H. Taylor, *ibid.*, 1971, 17.

6 Compounds that are skeletally related to (**4**) have been characterized as the alkali hydrolysis products of mexicanolide (**3**). See: J. D. Connolly, R. McCrindle, and K. H. Overton, *Chem. Commun.*, 1965, 162; *Tetrahedron*, 1967, **24**, 1489.