ภาคผนวก 2

ผลงานตีพิมพ์เผยแพร่

ผลงานตีพิมพ์

1. Thongdeeying, P., Chantrapromma, S., Fun, H.-K., Anjum, S., Ali, S., and Ponglimanont, C. 2005, "2-(9-Hydroxy-3a,5a,5b,8,8,11a-hexamethylicosahydro-1*H*-cyclopenta[a]chrysen-1-yl)propanoic acid (3β–hydroxylupan-29-oic acid), *Acta Cryst.*, E61, o1861-o1863.

2. Ponglimanont, C. and Thongdeeying, P. 2005. "Lupane-triterpene esters from the leaves of *Ceriops decandra* (Griff.) Ding Hou", *Aust. J. Chem.*, 58, 615-618.

ผลงานเผยแพร่

Thongdeeying, P., Ponglimanont, C., Karalai, C. and Chantrapromma, K. 2004. "Chemical constituents from the Leaves of *Ceriops decandra*", การประชุมวิชาการวิทยาศาสตร์และเทคโนโลยีแห่งประเทศไทย ครั้งที่ 30 19-21 ตุลาคม 2547 ณ ศูนย์แสดงสินค้าและการประชุมอิมแพ็ค เมืองทองธานี นำเสนอแบบโปสเตอร์

Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368
Editors: W. Clegg and D. G. Watson

2-(9-Hydroxy-3a,5a,5b,8,8,11a-hexamethylicosahydro-1*H*-cyclopenta-[*a*]chrysen-1-yl)propanoic acid (3β-hydroxylupan-29-oic acid)

Pakakrong Thongdeeying, Suchada Chantrapromma, Hoong-Kun Fun, Shazia Anjum, Shamsher Ali and Chanita Ponglimanont

Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2-(9-Hydroxy-3a,5a,5b,8,8,11a-hexamethylicosahydro-1*H*-cyclopenta[*a*]chrysen-1-yl)propanoic acid (3β-hydroxylupan-29-oic acid)

Pakakrong Thongdeeying,[a] Suchada Chantrapromma,[a]‡ Hoong-Kun Fun,[b]* Shazia Anjum,[c] Shamsher Ali[c] and Chanita Ponglimanont[a]

[a]Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand, [b]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [c]HEJ Research Institute of Chemistry, University of Karachi, Karachi 75270, Pakistan

‡ Additional correspondence author, email: suchada.c@psu.ac.th.

Correspondence e-mail: hkfun@usm.my

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.053
wR factor = 0.117
Data-to-parameter ratio = 8.4

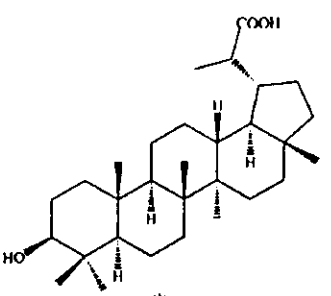
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 3 May 2005
Accepted 17 May 2005
Online 28 May 2005

The title compound, $C_{30}H_{50}O_3$, a lupane triterpene, was isolated from the leaves of *Ceriops decandra* (Griff.) Ding Hou. There are two crystallographically independent molecules in the asymmetric unit. In both molecules, the cyclopentane ring adopts an envelope conformation. In the crystal structure, molecules are interconnected into a two-dimensional network by intermolecular O—H···O hydrogen bonds.

Comment

Ceriops decandra (Griff.) Ding Hou (Rhizophoraceae) is a mangrove plant widely distributed from East Africa and Madagascar throughout tropical Asia and Queensland to Melanesia and Micronesia (Tomlinson, 1986). *C. decandra* has many local Thai names, *e.g.* Prong Khao and Prong Nu, and also a synonym of *Ceriops roxburghiana* Arn (Smitinand & Larsen, 1970). The bark of this plant has been used as a folk medicine for the treatment of diarrhoea, vomiting, amoebiasis and ulcers (Bamroongrugsa, 1999). An ethanol extract of the leaves has shown antinociceptive activity (Uddin *et al.*, 2005). The title compound, 3β-hydroxylupan-29-oic acid, (I), was previously isolated from *Gymnosporia wallichiana* (Kulshreshtha, 1977). As part of our research on bioactive compounds from Thai medicinal plants (Chantrapromma *et al.*, 2003, 2004; Waratchareeyakul *et al.*, 2004; Boonnak *et al.*, 2005), compound (I) was isolated for the first time from *Ceriops decandra* (Griff.) Ding Hou, collected from Phang-Nga province in the southern part of Thailand. We have undertaken the X-ray crystal structure analysis of (I) in order to establish its molecular structure and relative stereochemistry.



(I)

The asymmetric unit of (I) contains two crystallographically independent molecules, *A* and *B*, which have similar chiralities, bond lengths and angles (Fig. 1). The molecules are approximately related by a local twofold rotation axis. The bond lengths in (I) show normal values (Allen *et al.*, 1987). All the ring junctions in the lupane nucleus are *trans*-fused. In both molecules, the cyclohexane rings adopt chair conformations and the cyclopentane ring has an envelope conformation,

with atom C17 displaced from the C18/C22/C23/C24 plane by −0.692 (7) Å in molecule *A* and 0.674 (7) Å in molecule *B*. The hydroxyl group is equatorially attached at atom C3. The C23—C22—C25—C27 torsion angle of −55.1 (5)° [−45.7 (5)° in *B*] describes the orientation of the propanoic acid group with respect to the lupane nucleus. The C18—C22—C25—C26 torsion angle is −170.1 (4)° [−161.8 (3)° in *B*].

The molecular structure is stabilized by C—H···O hydrogen bonds (Table 2). O—H···O intermolecular hydrogen bonds link the molecules into a two-dimensional network parallel to the *ac* plane (Fig. 2).

Experimental

Air-dried leaves of *Ceriops decandra* (Griff.) Ding Hou (3.9 kg) were ground and extracted with hexane (2 × 20 l) at room temperature. The mixture was filtered and concentrated under reduced pressure to give a crude hexane extract (66.4 g). The crude extract was separated by quick column chromatography (QCC) on silica gel and eluted initially with hexane, followed by ethyl acetate and finally with methanol to give nine fractions (B1–B9). Fraction B7 (2.7 g) was subjected to column chromatography with MeOH–CH_2Cl_2 (0.2:9.8 *v*/*v*) and further purified by recrystallization from $CHCl_3$–EtOAc–MeOH (4:4:1) for a few days to obtain colourless single crystals of compound (I) [m.p. 518–520 K, $[\alpha]_D^{28}$ −42.6° (*c* = 0.125, MeOH)].

Crystal data

$C_{30}H_{50}O_3$	D_x = 1.103 Mg m^{-3}
M_r = 458.70	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 14 091 reflections
a = 8.1669 (8) Å	θ = 1.5–25.0°
b = 24.110 (2) Å	μ = 0.07 mm^{-1}
c = 14.4666 (14) Å	T = 293 (2) K
β = 104.057 (2)°	Plate, colourless
V = 2763.2 (4) Å^3	0.23 × 0.15 × 0.08 mm
Z = 4	

Data collection

Siemens SMART CCD area-detector diffractometer	4986 independent reflections
	3296 reflections with $I > 2\sigma(I)$
ω scans	R_{int} = 0.050
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	θ_{max} = 25.0°
	$h = -9 \rightarrow 9$
T_{min} = 0.988, T_{max} = 0.994	$k = -23 \rightarrow 28$
14 091 measured reflections	$l = -14 \rightarrow 17$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0486P)^2 + 0.1104P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.053	
$wR(F^2)$ = 0.117	
S = 1.02	$(\Delta/\sigma)_{max} < 0.001$
4986 reflections	$\Delta\rho_{max}$ = 0.16 e Å^{-3}
596 parameters	$\Delta\rho_{min}$ = −0.14 e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

O1*A*—C3*A*	1.452 (5)	O1*B*—C3*B*	1.445 (5)
O2*A*—C27*A*	1.234 (6)	O2*B*—C27*B*	1.236 (5)
O3*A*—C27*A*	1.264 (5)	O3*B*—C27*B*	1.284 (5)
O2*A*—C27*A*—O3*A*	122.9 (5)	O2*B*—C27*B*—O3*B*	123.8 (5)
O3*A*—C27*A*—C25*A*	118.1 (5)	O3*B*—C27*B*—C25*B*	116.0 (4)

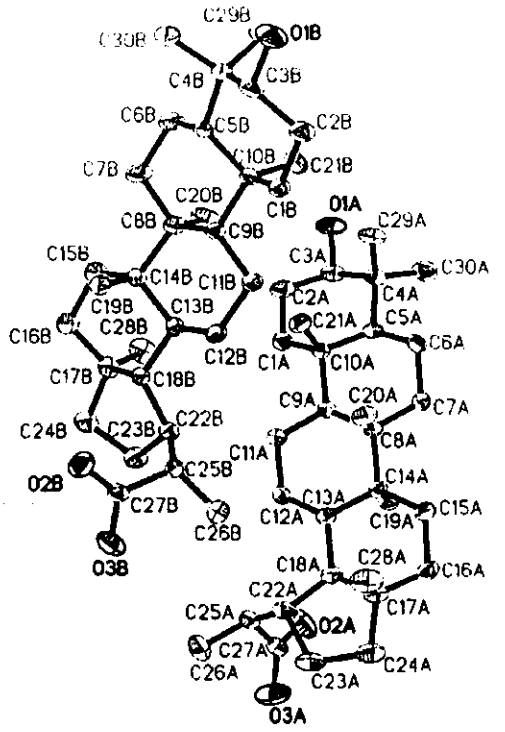


Figure 1
The asymmetric unit of (I), showing 30% probability displacement ellipsoids and the atomic numbering. For clarity, H atoms have been omitted.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*A*—H1*A*···O2*B*^{i}	0.82	1.91	2.705 (6)	161
O1*B*—H1*D*···O2*A*^{ii}	0.82	1.86	2.662 (6)	165
O3*A*—H3*A*···O1*A*^{iii}	0.82	1.98	2.724 (6)	151
O3*B*—H3*C*···O1*B*^{iv}	0.82	1.82	2.625 (5)	163
C18*A*—H18*A*···O2*A*^{v}	0.98	2.52	3.262 (6)	132
C18*B*—H18*B*···O2*B*^{v}	0.98	2.46	3.206 (5)	133
C23*A*—H23*B*···O3*A*^{v}	0.97	2.49	3.222 (7)	132
C23*B*—H23*D*···O3*B*^{v}	0.97	2.49	3.237 (6)	134
C30*A*—H30*A*···O1*A*^{v}	0.96	2.56	2.957 (7)	105
C30*B*—H30*D*···O1*B*^{v}	0.96	2.51	2.917 (7)	105

Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z$; (ii) $-x, y-\frac{1}{2}, -z$; (iii) $x, y, z+1$; (iv) $x+1, y, z+1$; (v) x, y, z.

H atoms were placed in calculated positions, with O—H distances of 0.82 Å and C—H distances in the range 0.93–0.98 Å. The U_{iso} values were constrained to be $1.5U_{eq}$ of the carrier atom for hydroxyl and methyl H atoms, and $1.2U_{eq}$ for the remaining H atoms. In the absence of significant anomalous dispersion effects, Friedel pairs were merged before the final refinement and the absolute configuration was assigned arbitrarily.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

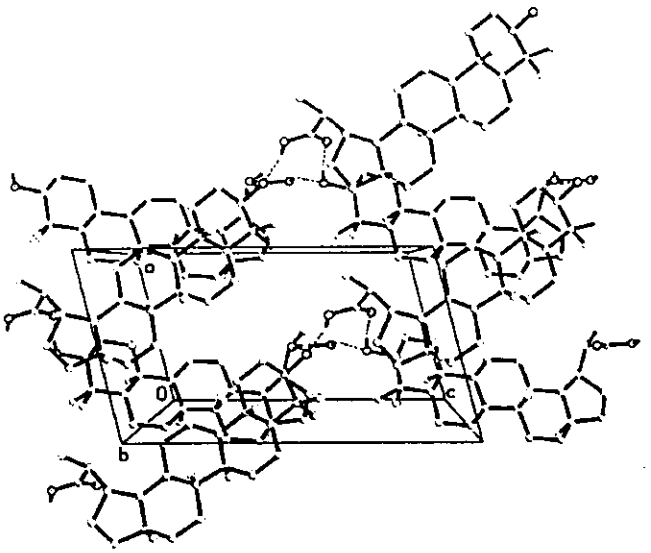


Figure 2
A view of the packing of (I). Only hydroxyl H atoms are shown. O–H···O hydrogen bonds are shown as dashed lines.

PT thanks the Higher Education Development Project: Postgraduate Education and Research Program in Chemistry for financial support. The authors thank Prince of Songkla University and the Pakistan Government, and also the Malaysian Government and Universiti Sains Malaysia for the Scientific Advancement Grant Allocation (SAGA) grant No. 304/PFIZIK/653003/A118.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bamroongrugsa, N. (1999). *Songklanakarin J. Sci. Technol.* **21**, 377–386.
Boonnak, N., Chantrapromma, S., Fun, H.-K., Anjum Ali, S., Rahman, A. & Karalai, C. (2005). *Acta Cryst.* E**61**, o410–o412.
Chantrapromma, S., Fun, H.-K., Ibrahim, A. R., Laphookhieo, S. & Karalai, C. (2003). *Acta Cryst.* E**59**, o1864–o1866.
Chantrapromma, K., Saewan, N., Fun, H.-K., Chantrapromma, S. & Rahman, A. A. (2004). *Acta Cryst.* E**60**, o312–o314.
Kulshreshtha, D. K. (1977). *Phytochemistry*, **16**, 1783–1785.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Smitinand, T. & Larsen, K. (1970). *Flora of Thailand*, Vol. 2, Part 1, pp. 10–12. Bangkok: The ASRCT Press.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Tomlinson, P. B. (1986). *The Botany of Mangroves*, pp. 352–357. Cambridge University Press.
Uddin, S. J., Shilpi, J. A., Barua, J. & Rouf, R. (2005). *Fitoterapia*, **76**, 261–263.
Waratchareeyakul, W., Chantrapromma, S., Fun, H.-K., Razak, I. A., Karalai, C. & Ponglimanont C. (2004). *Acta Cryst.* E**60**, o1964–o1966.

CSIRO PUBLISHING

Short Communication

www.publish.csiro.au/journals/ajc

Aust. J. Chem. 2005, *58*, 615–618

Lupane-Triterpene Esters from the Leaves of *Ceriops decandra* (Griff.) Ding Hou

Chanita Ponglimanont[A,B] *and Pakakrong Thongdeeying*[A]

[A] Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand.

[B] Corresponding author. Email: chanita.p@psu.ac.th

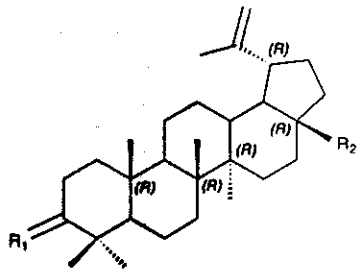
Two novel triterpene esters were isolated from the leaves of *Ceriops decandra* in addition to 16 known triterpenes: lupenone **3**, lupeol **4**, betulinaldehyde **5**, 3β-*Z*-coumaroyllupeol **6**, 3β-*E*-coumaroyllupeol **7**, 3-*epi*-betulinic acid **8**, betulin **9**, betulinic acid **10**, 3β-*E*-feruloylbetulin **11**, 30-nor-lup-3β-ol-20-one **12**, 3β-*E*-caffeoyllupeol **13**, lup-20(29)-en-3β,30-diol **14**, 3β-hydroxylupan-29-oic acid **15**, 3β,20-dihydroxylupane **16**, and a mixture of oleanolic and ursolic acid **17** and **18**. The new compounds were determined by spectroscopic methods to be 3β-*E*-feruloyllupeol **1** and 3β-*Z*-feruloyllupeol **2**. Compounds **3** and **5**–**16** were reported for the first time as metabolites of *C. decandra*.

Manuscript received: 1 April 2005.
Final version: 3 July 2005.

The genus Ceriops (Rhizophoraceae) is comprised of two species: *Ceriops decandra* (Griff.) Ding Hou and *Ceriops tagal* (Perr.) C. B. Robinson. They are mangrove plants widely distributed from East Africa and Madagascar, throughout tropical Asia and Queensland, to Melanesia and Micronesia.[1] *C. decandra* has many local Thai names: Prong Khao, Prong Nu, and also a synonym of *Ceriops roxburghiana* Arn.[2] Its bark has been used as a folk medicine for the treatment of diarrhea, vomiting, amoebiasis, and ulcers.[3] Various parts of *C. decandra* have been phytochemically studied. Methanol extracts of the bark yielded D-catechin, leucoanthocyanidins,[4] and procyanidin.[5] Leaf extracts yielded α-amyrin, β-amyrin, lupeol, oleanolic acid, and ursolic acid.[6] Anjaneyulu et al. have isolated ceriopsin A–D,[7] ceriopsin E,[8] and ceriopsin F and G[9] from the roots. In this present study, the hexane extract from leaves has been investigated, which resulted in the isolation of two new triterpene esters **1** and **2** along with 16 known triterpenes (Fig. 1): lupenone **3**,[10] lupeol **4**,[11] betulinaldehyde **5**,[12] 3β-*Z*-coumaroyllupeol **6**,[13] 3β-*E*-coumaroyllupeol **7**,[14] 3-*epi*-betulinic acid **8**,[14] betulin **9**,[15] betulinic acid **10**,[12] 3β-*E*-feruloylbetulin **11**,[16] 30-nor-lup-3β-ol-20-one **12**,[17] 3β-*E*-caffeoyllupeol **13**,[18] lup-20(29)-en-3β,30-diol **14**,[19] 3β-hydroxylupan-29-oic acid **15**,[20] 3β,20-dihydroxylupane **16**,[21] and a mixture of oleanolic and ursolic acid **17**, **18**.[22] The structures of the compounds were elucidated by comparison of their physical and spectroscopic data with reported values.

Compound **1** was obtained as a white solid. Its electrospray ionization time-of-flight (ESI TOF) mass spectrum showed the $[M - H]^-$ ion peak at *m/z* 601.4244, corresponding to the molecular formula $C_{40}H_{58}O_4$. The IR spectrum suggested hydroxy (3534 cm^{-1}), double bond (1635, 1604 cm^{-1}), and conjugated ester (1703 cm^{-1}) functionalities. This compound exhibited UV absorption maxima at 234, 298, and 325 nm, again suggesting the presence of conjugation in the molecule. It gave a purple vanillin–sulfuric acid test indicating a triterpene. The ^1H NMR spectra of **1** supported the presence of a *trans*-feruloyl substituent as three 1,2,4-trisubstituted aromatic protons at δ_H 6.91 (1H, d, *J* 8.1, H8′), 7.03 (1H, d, *J* 1.8, H5′), and 7.07 (1H, dd, *J* 8.1, 1.8, H9′), two *trans*-oriented vinyl protons at δ_H 6.29 and 7.59 (each d, *J* 15.9, H2′ and H3′, respectively), and aromatic methoxy protons at δ_H 3.93 (3H, s) were observed.[23] A signal of a hydroxy proton (which disappeared upon D_2O exchange) was observed at δ_H 5.85 (1H, s). A cross peak between H5′ and the aromatic OMe observed by NOESY located the latter at position C6′.[16,23] A lupane triterpenoid skeleton was evident from the following ^1H NMR signals: six methyl groups at δ_H 0.79, 0.88, 0.89, 0.92, 0.95, and 1.04 (3H, s, each), an isopropenyl group [δ_H 1.69 (3H, s), 4.60 (1H, m), 4.69 (1H, d, *J* 2.1)],[23] and a typical lupane H_β-19 proton at δ_H 2.37 (1H, m).[24] An oxymethine proton in proximity to an ester moiety was observed at δ_H 4.62 (dd, *J* 9.0, 5.4, H3). The doublet-of-doublets splitting pattern, together with the large coupling constant of H3 with J_{ax-ax} 9.0 and J_{ax-eq} 5.4 indicated an axial (α-) orientation of H3. The ester carbonyl was also confirmed by a ^{13}C NMR signal at δ_C 167.1. The ester substituent was placed at C3 as a result of a downfield shift observed for H3 and C3 in the ^1H and ^{13}C NMR spectra, respectively, compared with analogous data from lupeol,[11] and from the correlations between H3 (δ_H 4.62) and C23 (δ_C 28.0), C24 (δ_C 16.2), and C1′ (δ_C 167.1) observed in the HMBC spectrum. The ^{13}C NMR signals for sp^2 methine carbons were

10.1071/CH05087 0004-9425/05/080615



1: R_1 = H, β-O-*E*-feruloyl $R_2 = CH_3$

2: R_1 = H, β-O-*Z*-feruloyl $R_2 = CH_3$

3: R_1 = O $R_2 = CH_3$

4: R_1 = H, β-OH $R_2 = CH_3$

5: R_1 = H, β-OH $R_2 = CHO$

6: R_1 = H, β-O-*Z*-coumaroyl $R_2 = CH_3$

7: R_1 = H, β-O-*E*-coumaroyl $R_2 = CH_3$

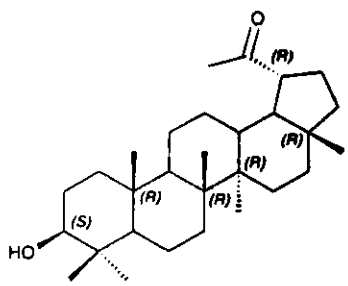
8: R_1 = H, α-OH $R_2 = COOH$

9: R_1 = H, β-OH $R_2 = CH_2OH$

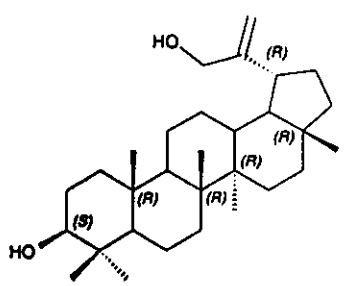
10: R_1 = H, β-OH $R_2 = COOH$

11: R_1 = H, β-O-*E*-feruloyl $R_2 = CH_2OH$

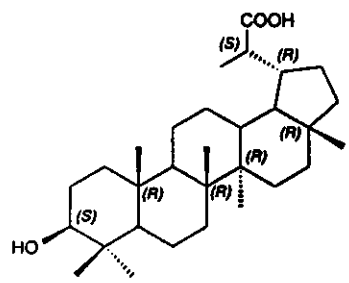
13: R_1 = H, β-O-*E*-caffeoyl $R_2 = CH_3$



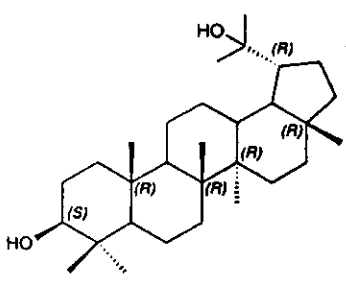
12



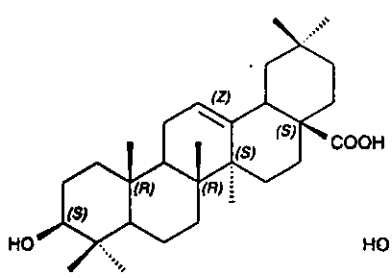
14



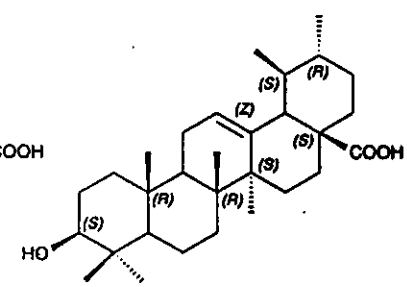
15



16



17



18

Fig. 1. Structures of compounds 1–18.

shown at δ_C 116.3 (C2′), 144.3 (C3′), 109.3 (C5′), 114.7 (C8′), and 123.1 (C9′), and one olefinic methylene carbon at δ_C 109.4 (C29). In addition, seven methyls, one methoxy, 11 methylenes, 11 methines, and 10 quaternary carbon signals were characterized by a DEPT experiment. Therefore, compound **1** was assigned as 3β-*E*-feruloyllupeol.

Compound **2** was obtained as a white solid. Its ESI TOF mass spectrum showed the $[M-H]^-$ ion peak at *m/z* 601.4260, which corresponds to the molecular formula $C_{40}H_{58}O_4$. The ^1H and ^{13}C NMR spectroscopic data (Tables 1 and 2) were closely related to those of **1**, except for the olefinic proton signals at δ_H 5.81 (1H, d, *J* 12.9) and 6.77 (1H, d, *J* 12.9) assignable, respectively, to H2′ and H3′ on the feruloyl group. Judging from the small *J* value (12.9), the double bond should have a *Z* geometry. These spectroscopic data implied a lupeol bearing a *Z*-feruloyl group. On the basis of HMBC, the *Z*-feruloyl moiety was located at C3 by correlation of the H3 signal (δ_H 4.54) with C1′ (δ_C 166.4), C23 (δ_C 28.0), and C24 (δ_C 16.2). The coupling constant and splitting pattern of H3 (dd, *J* 11.1, 5.4) indicated an α-orientation of H3. Hence, compound **2** was assigned as 3β-*Z*-feruloyllupeol.

It is worth noting that the leaf extract of *C. decandra* contains mainly lupane triterpenoids, a lupeol, and its derivatives. The latter arise from oxidation of Me-28 of a 3β-lupeol (**9**, **5**, **10**) or Me-30 (**14**) or either esterification of the 3β-OH group of a lupeol itself (**1**, **2**, **6**, **7**, **13**) or its oxidized metabolite

Table 1. ^{1}H NMR data for compounds 1 and 2 (300 MHz, $CDCl_3$)

Position	1[A] δ_H, mult., J [Hz]	2[A] δ_H, mult., J [Hz]
3	4.62, dd, 9.0, 5.4	4.54, dd, 11.1, 5.4
19	2.37, m	2.38, m
23	0.88, s	0.86, s
24	0.89, s	0.81, s
25	0.92, s	0.86, s
26	1.04, s	1.03, s
27	0.95, s	0.94, s
28	0.79, s	0.79, s
29	4.69, d, 2.1	4.69, d, 2.1
	4.60, m	4.57, m
30	1.69, s	1.69, s
2′	6.29, d, 15.9	5.81, d, 12.9
3′	7.59, d, 15.9	6.77, d, 12.9
5′	7.03, d, 1.8	7.78, d, 1.8
8′	6.91, d, 8.1	6.87, d, 8.4
9′	7.07, dd, 8.1, 1.8	7.10, dd, 8.4, 1.8
OMe	3.93, s	3.91, s
OH	5.85, s	5.88, s

[A] Determined by HMQC NMR spectroscopy.

Table 2. ^{13}C NMR data for compounds 1 and 2 (75 MHz, $CDCl_3$)

Position	1, δ_C	2, δ_C	Position	1, δ_C	2, δ_C
1	38.5	38.5	21	29.9	29.9
2	23.9	23.8	22	40.0	40.0
3	80.9	80.7	23	28.0	28.0
4	38.1	37.1	24	16.2	16.2
5	55.5	55.5	25	16.7	16.5
6	18.3	18.3	26	16.0	16.0
7	34.3	34.3	27	14.6	14.5
8	40.9	40.9	28	18.0	18.0
9	50.4	50.4	29	109.4	109.4
10	37.2	37.9	30	19.3	19.4
11	21.0	21.0	1′	167.1	166.4
12	25.2	25.1	2′	116.3	117.4
13	38.1	38.1	3′	144.3	143.5
14	42.9	43.0	4′	127.2	127.3
15	27.5	27.5	5′	109.3	112.9
16	35.6	35.6	6′	146.8	146.0
17	43.0	42.8	7′	147.8	147.0
18	48.3	48.3	8′	114.7	113.9
19	48.0	48.0	9′	123.1	125.6
20	151.0	150.9	OMe	56.0	56.0

11. Addition of H_2O to a double bond at C20–C29 of a 3β-lupeol gives 16. Oxidation of a primary alcohol at C30 of 14 and hydrogenation of a double bond at C20–C29 yields 15, whereas oxidative cleavage of this same double bond affords 12. A lupenone 3 can be derived from oxidation of a 3β-OH group of a lupeol, which may subsequently be reduced to a 3α-OH group and somehow undergo further oxidation at Me-28 to give 8.

Experimental

General Procedures

Melting points were determined on an Electrothermal melting point apparatus. UV spectra were measured with a SPECORD S 100 (Analytikjena). The IR spectra were measured with a FTS FT-IR Perkin Elmer spectrophotometer. NMR spectra were obtained with a Bruker FT-NMR Ultra Shield spectrometer [^{1}H (300 MHz) and ^{13}C (75 MHz)]. Chemical shifts were recorded in δ (ppm) in $CDCl_3$. ESI TOF mass spectra were performed using a Micromass LCT mass spectrometer. The $[\alpha]_D$ values were determined with an AUTOPOL^R II automatic polarimeter. Column chromatography (CC) and quick column chromatography (QCC) were carried out on silica gel 100 and 60H, respectively. Precoated plates of silica gel 60 F_{254} (Merck) were used for analytical purposes.

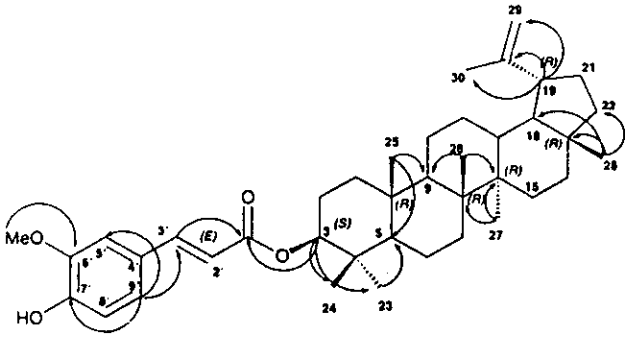


Fig. 2. Selected HMBC correlations of 1.

Plant Material

Leaves of *Ceriops decandra* (Griff.) Ding Hou were collected from Phang-nga province, Thailand, in March 2003. The plant was identified by Dr Kitichate Sridith and a voucher specimen (collection No. K. Chantrapromma 1/46 (PSU)) was deposited in the herbarium of the Department of Biology, Faculty of Science, Prince of Songkla University, Songkhla, Thailand.

Extraction and Isolation

Air-dried ground leaves of *C. decandra* (3.9 kg) were extracted twice with hexane (2 × 20 L, for 5 days each) at room temperature. The mixture was filtered and concentrated under reduced pressure to give a white green solid (23.1 g) and the crude hexane extract (66.4 g). The solid was further purified by QCC with hexane and the polarity increased with CH_2Cl_2 and MeOH to give 4 (5.1 g) and eight fractions (A1–A8).

Fraction A3 (150.9 mg) was purified by CC using EtOAc/hexane (0.5 : 9.5) to give 5 (3.5 mg). Fraction A6 was washed with dichloromethane to give a pale yellow solid (705.0 mg) which was purified by CC with CH_2Cl_2/hexane (7 : 3) to give 9 (263.7 mg) and 10 (46.9 mg). Fraction A8 was separated by CC (CH_2Cl_2/hexane, 8 : 2) to afford a mixture of 17 and 18 (12.2 mg). The crude hexane extract (66.4 g) was subjected to QCC with hexane and the polarity increased with CH_2Cl_2 and MeOH to give 4 (21.4 g) and eight fractions (B1–B8). Fraction B2 (12.4 g) was subjected to QCC using gradient elution of hexane/EtOAc and further purified by CC (EtOAc/hexane, 0.2 : 9.8) to afford 3 (67.3 mg). Fraction B4 (7.1 g) was subjected to QCC (EtOAc/hexane, 1.5 : 8.5) to afford 8 (38.7 mg) and two subfractions: B4a, (4.2 g), B4b (961.9 mg). Subfraction B4a was further purified by CC using EtOAc/hexane (1 : 9) to give 6 (2.6 mg) and 7 (381.9 mg). Subfraction B4b was separated by CC (EtOAc/hexane, 0.5 : 9.5) and further purified by preparative layer chromatography (PLC) with EtOAc/hexane (7 : 3) to afford 1 (5.5 mg) and 2 (6.0 mg). Fraction B6 (5.1 g) was subjected to QCC (gradient of 100% hexane to 100% EtOAc) to give two subfractions. Subfraction B6a (1.1 g) was purified by CC (acetone/hexane, 2 : 8) and further purified by QCC with acetone/hexane (1 : 9) to afford 12 (62.4 mg). Subfraction B6b (578.6 mg) was subjected to QCC using acetone/hexane (1 : 9) and further purified by CC and PLC (acetone/CH_2Cl_2, 0.5 : 9.5) to afford 13 (23.3 mg). Fraction B7 (2.7 g) was purified by CC with MeOH/CH_2Cl_2 (0.2 : 9.8) and further separated by CC (acetone/hexane, 2 : 8) to give 11 (16.4 mg) and subfraction B7a (2.0 g), which was further purified by CC with acetone/CH_2Cl_2 (0.3 : 9.7) to afford 14 (23.8 mg), 15 (5.9 mg), and 16 (13.1 mg).

3β-*E*-Feruloyllupeol 1: white solid, mp 167–169°C. ν_{max} (KBr)/cm^{-1} 3534 (OH), 1703 (C=O), 1635, 1604 (C=C). λ_{max}/nm (MeOH) (log ε): 234 (4.02), 298 (4.06), 325 (4.20). *m/z* (ESI TOF) 601.4244 [M − H]$^-$, Calcd. for $C_{40}H_{57}O_4$: 601.4256. $[\alpha]_D^{27}$ +140° (*c* 0.025, $CHCl_3$). ^{1}H NMR (300 MHz in $CDCl_3$) and ^{13}C NMR (75 MHz in $CDCl_3$) see Tables 1 and 2, respectively.

3β-*Z*-Feruloyllupeol 2: white solid, mp 195–197°C. ν_{max} (KBr)/cm^{-1} 3538 (OH), 1708 (C=O), 1610, 1595 (C=C). λ_{max}/nm (MeOH) (log ε): 235 (3.57), 296 (3.58), 325 (3.71). *m/z* (ESI TOF) 601.4260 [M − H]$^-$, Calcd. for $C_{40}H_{57}O_4$: 601.4256. $[\alpha]_D^{27}$ +41.66° (*c* 0.060, $CHCl_3$). ^{1}H NMR (300 MHz in $CDCl_3$) and ^{13}C NMR (75 MHz in $CDCl_3$) see Tables 1 and 2, respectively.

Acknowledgments

We thank the Higher Education Development Project: Postgraduate Education and Research Program in Chemistry, funded by the Royal Thai Government, the Graduate School, the Natural Products from Mangrove Plants and Synthetic Materials Research Unit, and the Prince of Songkla University for financial support.

References

[1] P. B. Tomlinson, *The Botany of Mangroves* **1986**, pp. 352–357 (Cambridge University Press: Cambridge).
[2] T. Smitinand, K. Larsen, *Flora of Thailand* **1970**, Vol. 2, pp. 10–12 (ASRCT Press: Bangkok).
[3] N. Bamroongrugsa, *Songklanakarin J. Sci. Technol.* **1999**, *21*, 377.
[4] D. Ghosh, S. K. Barat, *Leather Science (Madras)* **1963**, *10*, 403.
[5] T. R. Seshadri, R. K. Trikha, *Ind. J. Chem.* **1971**, *9*, 928.
[6] A. Ghosh, S. Misra, A. K. Dutta, A. Choudhury, *Phytochemistry* **1985**, *24*, 1725. doi:10.1016/S0031-9422(00)82541-8
[7] A. S. R. Anjaneyulu, V. L. Rao, *Phytochemistry* **2002**, *60*, 777. doi:10.1016/S0031-9422(02)00087-0
[8] A. S. R. Anjaneyulu, V. L. Rao, E. Lobkovsky, J. Clardy, *J. Nat. Prod.* **2002**, *65*, 592. doi:10.1021/NP010540P
[9] A. S. R. Anjaneyulu, V. L. Rao, *Phytochemistry* **2003**, *62*, 1207. doi:10.1016/S0031-9422(02)00627-1
[10] T. K. Razdan, S. Harkar, B. Qadri, M. A. Qurishi, M. A. Khuroo, *Phytochemistry* **1988**, *27*, 1890. doi:10.1016/0031-9422(88)80473-4
[11] W. F. Reynolds, S. McLean, J. Poplawski, *Tetrahedron* **1986**, *42*, 3419. doi:10.1016/S0040-4020(01)87309-9
[12] F. A. Macias, A. M. Simonet, M. D. Esteban, *Phytochemistry* **1994**, *36*, 1369. doi:10.1016/S0031-9422(00)89726-5
[13] M. Ali, A. Heaton, D. Leach, *J. Nat. Prod.* **1997**, *60*, 1150. doi:10.1021/NP9700580
[14] T. V. Sung, W. Steglich, G. Adam, *Phytochemistry* **1991**, *30*, 2349. doi:10.1016/0031-9422(91)83647-4
[15] W. F. Tinto, L. C. Blair, A. Alli, *J. Nat. Prod.* **1992**, *55*, 395. doi:10.1021/NP50081A020
[16] Y. H. Kuo, C. I. Chang, Y. H. Kuo, *Phytochemistry* **1997**, *46*, 1135. doi:10.1016/S0031-9422(97)00227-6
[17] S. Koul, T. K. Razdan, C. S. Andotra, A. K. Kalla, S. Koul, S. C. Taneja, K. L. Dhar, *Phytochemistry* **2000**, *53*, 305. doi:10.1016/ S0031-9422(99)00490-2
[18] N. Alvarenga, E. A. Ferro, *Fitoterapia* **2000**, *71*, 719. doi:10.1016/S0367-326X(00)00217-3
[19] M. Abdel-Mogib, *Phytochemistry* **1999**, *51*, 445. doi:10.1016/S0031-9422(98)00771-7
[20] D. K. Kulshreshtha, *Phytochemistry* **1977**, *16*, 1783. doi:10.1016/0031-9422(71)85089-6
[21] A. Yuruker, J. Orjala, O. Sticher, T. Rali, *Phytochemistry* **1998**, *48*, 863. doi:10.1016/S0031-9422(97)00901-1
[22] W. Seebacher, N. Simic, R. Weis, R. Saf, O. Kunert, *Magn. Reson. Chem.* **2003**, *41*, 636. doi:10.1002/MRC.1214
[23] B. Y. Hwang, H.-B. Chai, L. B. S. Kardono, S. Riswan, N. R. Farnworth, G. A. Cordell, J. M. Pezzuto, A. D. Kinghorn, *Phytochemistry* **2003**, *62*, 197. doi:10.1016/S0031-9422(02)00520-4
[24] G. Culioli, C. Mathe, P. Archier, C. Vieillescazes, *Phytochemistry* **2003**, *62*, 537. doi:10.1016/S0031-9422(02)00538-1

บทคัดย่อ
ABSTRACTS

การประชุมวิชาการ
วิทยาศาสตร์และเทคโนโลยีแห่งประเทศไทย ครั้งที่ 30

19-21 ตุลาคม 2547

ณ ศูนย์แสดงสินค้าและการประชุมอิมแพ็ค เมืองทองธานี

30th Congress on Science and Technology of Thailand

19-21 October 2004

Impact Exhibition and Convention Center , Muang Thong Thani

สมาคมวิทยาศาสตร์แห่งประเทศไทยในพระบรมราชูปถัมภ์
THE SCIENCE SOCIETY OF THAILAND
UNDER THE PATRONAGE OF HIS MAJESTY THE KING

คณะวิทยาศาสตร์ มหาวิทยาลัยศรีนครินทรวิโรฒ
FACULTY OF SCIENCE
SRINAKARINWIROT UNIVERSITY

C

C0001-Chemical Constituents from the Leaves of *Ceriops decandra*

Pakakrong Thongdeeying[1], Chanita Ponglimanont[1], Chatchanok Karalai[1] and Kan Chantrapromma[2]
[1]Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-yai, Songkhla 90112, Thailand.
[2] Institute of Science, Walailak University, Thasala, Nakhon Si Thammarat 80160, Thailand.
E-mail address: s4622054@maliwan.psu.ac.th

Abstract: Air-dried ground leaves of *Ceriops decandra* (Griff.) Ding Hou (Rhizophoraceae) were extracted with hexane, methylene chloride and acetone, successively. The crude hexane extract was separated by chromatographic techniques to yield eight lupane-type triterpenes: Lupeol (1), Betulinaldehyde (2), 3β-(Z)-Coumaroyl lupeol (3), 3β-(E)-Coumaroyl lupeol (4), 3-*epi*-Betulinic acid (5), Betulin (6), Betulinic acid (7), and 3β-(E)-Feruloyl betulin (8). Their structures were determined by spectroscopic methods (IR, UV, NMR).