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CONSTITUENTS OF *CLINACANTHUS NUTANS* AND THE CRYSTAL STRUCTURE OF LUP-20(29)-ENE-3-ONE

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Summary

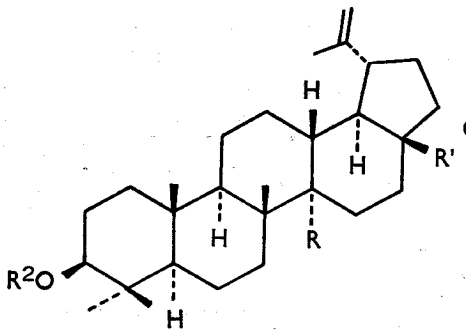
Lupeol and "β-sitosterol" have been isolated from the stems of ***Clinacanthus nutans*** *(Burn) Lindau (****C. siamensis*** *Bremek.) The crystal structure of lup-20(29)-ene-3-one, prepared by oxidation of lupeol, has been determined by X-ray diffraction at 295 K and refined by least squares to a residual of 0.075 for 1507 "observed" reflections. Crystals are orthorhombic* $P2_12_12_1$, $a = 17.318(9)$, $b = 13.999(7)$, $c = 10.602(4)$ Å, $Z = 4$. *The geometry of the polycyclic skeleton is closely akin to those previously reported for methyl melateucate iodoacetate and 3-β-acetoxy-20-hydroxylupane.*

Introduction

The genus *Clinacanthus* comprises two species and belongs to the family Acanthaceae[1,2]. *C. nutans* (Burn) Lindau (*C. siamensis* Bremek) is a small shrub which occurs throughout South East Asia; in Thailand it is known as เสลดพังพอน. In folk medicine the plant has been esteemed as a remedy for snake bite but neither Levey[3] nor Ratanabanangoon[4] has found any evidence to support this claim.

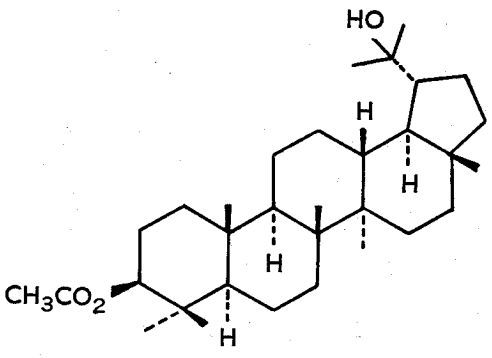
In the present work, chromatography of a light petroleum extract of the stems of *C. nutans* has yielded lupeol(1) and "β-sitosterol". Lupeol(1) was identified by comparison with an authentic specimen and, in addition, was characterized by oxidation to lup-20(29)-ene-3-one(4). The crystal structure of (4) was determined in order to compare its molecular geometry with those of methyl melaleucate iodoacetate(2)[5] and 3β-acetoxy-20-hydroxylupane(3)[6] which appear to be the only other derivatives of lupane investigated by X-ray crystallographic analysis.

Further work on other constituents of *Clinacanthus* species is in progress.

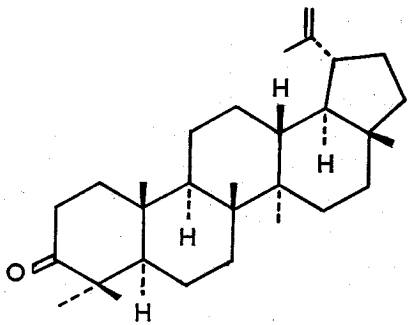


(1) R' = CH_3, R^2 = H

(2) R' = CO_2CH_3, R^2 = $COCH_2I$



(3)



(4)

Experimental

Nuclear magnetic resonance (n.m.r.) spectra were determined with a Varian A-60-D Spectrometer operating at 60 MHz, using tetramethylsilane ($\delta = 0.00$) as an internal standard. Infrared (i.r.) spectra were measured with a Perkin Elmer 237 Infracord. Mass spectra were determined with a Varian MAT CH7 instrument. Melting points are uncorrected.

C. nutans was collected near Haad-Yai in August 1975 and again near Kasetsart University in December 1975 and was shade dried. The milled stems (2.0 kg) were extracted exhaustively with light petroleum in a Soxhlet apparatus then the extract was evaporated. The resulting dark oil (24.0 g) was chromatographed on a column of silica gel (960 g).

Elution of the column with light petroleum followed by mixtures of ether (2-10%) and light petroleum yielded a number of waxy fractions. These evidently contained long chain compounds (n.m.r., i.r., and mass spectra) and they were not examined further.

Elution of the column with 10-20% ether/light petroleum then gave a residue (4.7 g) which was purified further by preparative layer chromatography on silica gel using ethyl acetate/light petroleum (1:9) as the developing solvent. Crystallization

of the product from ether/light petroleum yielded lupeol(1) as needles (3.7 g) m.p. 207-8° not depressed on admixture with an authentic specimen (lit[7] 211-2°). Oxidation of lupeol(1) (213 mg) with chromium trioxide (300 mg) in pyridine (1 ml) and methylene chloride (8 ml) at room temperature for 2 h gave lup-20(29)-ene-3-one(4) which crystallized from methanol/ether as prisms (197 mg) m.p. 167-8° (lit.[7] 169.5-170.5°).

Further elution of the column with 20-40% ether/light petroleum mixtures gave a residue (2.6 g) which was rechromatographed on a column of neutral alumina. The product, which gave a positive Burchard-Liebermann test, was eluted with mixtures of ether and light petroleum and was crystallized from aqueous methanol whereupon "β-sitosterol" was obtained as plates m.p. 140-1° (lit.[8] 137-8°). The acetate had m.p. 130-2° (lit.[8] 125.6°) and the benzoate had m.p. 145-7° (lit.[8] 147-8°).

Crystallography

Single crystals of a size and habit suitable for X-ray crystallographic examination and structure determination were grown by slow cooling of a methanol/ether solution and were obtained as thick needles elongated along *c*. Approximate cell dimensions were obtained from a preliminary photographic examination using rotation and Weissenberg exposures and the probable space group was established as $P2_12_12_1$ from the observed systematic absences. A prismatic needle section $0.18 \times 0.18 \times 0.32$ mm (*a*, *b*, *c*) was mounted on a quartz fibre with *c* parallel to the fibre axis and, after ensuring satisfactory reflection and crystal quality by photographic methods, it was transferred to the goniometer head of a Syntex $P\bar{1}$ computer-controlled four-circle diffractometer, at the controlled ambient temperature of 295(1) K. Molybdenum K(α) radiation was used for data collection and cell determination. A perpendicularly-oriented graphite crystal incident beam monochromator was used, the tube take-off angle being 4°, with λ assumed to be 0.71069 Å. The scintillation counter, with a pulse height discriminator adjusted to pass approximately 95% of the K($\bar{\alpha}$) peak, was positioned 19 cm from the crystal, a coincidence correction being automatically applied for very intense reflections. The standard program system accompanying the instrument was used for crystal orientation, least squares cell determination, and data collection. A rotation photograph was taken with a stationary film mounted 9.8 cm from the crystal in front of the counter and used to locate 15 reflections which were then automatically centred in the counter aperture and used to determine a preliminary crystal orientation matrix. Fifteen further reflections with $2\theta \sim 30°$ were then located in a wide range of reciprocal space; a final orientation matrix, and cell dimensions were obtained from the centred reflections. The mosaic width of a number of low angle reflections were examined and the half-width found to be uniformly 0.4°. A unique data set was then measured using a $2\theta/\theta$ scan technique at a fixed scan rate of 2° min^{-1}. The scan width was set at 1.5°, an automatically applied increment being added to correct for the splitting of the K($\alpha_{1,2}$) components. Stationary crystal—stationary counter backgrounds equal to half the scan time were recorded at either limit of the scan, the background being assumed to vary linearly over the width. The net integrated intensity, *I*, and its standard deviation $\sigma(I)$ were determined by the relationships

$$I = [C - 0.5(t_c/t_b)\ (B_1 + B_2)]$$
$$\sigma(I) = [C - 0.25(t_c/t_b)^2\ (B_1 + B_2)]^{1/2},$$

C being the integrated peak count, t_c the scan time, t_b the total background counting time, and B_1 and B_2 the background counts at either end of the scan. Intensities were measured for all unique reflections with a 2θ limit of 45°, previous examination having shown this to be the effective limit of observable data. As a control on crystal decomposition and electronic and orientation stability, three axial reflections (600, 040, 006) were measured every 100 reflections but no significant variation in intensity or peak centring was found.

The measured data were then corrected for Lorentz and polarization factors; the low absorption coefficient of the crystal implied variations of μR to be negligible within the accuracy of the experiment and no absorption correction was applied. Of the 1904 independent measured reflections, 1507 for which $I > 2\sigma(I)$ were considered 'observed' and used in the structure refinement after the structure had been solved initially using the complete data set.

Crystal Data: $C_{30}H_{48}O$, $M = 424.7$, orthorhombic, space group $P2_12_12_1$ (International Tables for X-ray Crystallography Vol. 1, No. 19, D_2^4), $a = 17.318(9)$, $b = 13.999(7)$, $c = 10.602(4)$Å, $U = 2570(3)$Å^3, D_m (determined by neutral buoyancy in KI/water) = 1.10, $D_c = 1.10$ g cm^{-3} for $Z = 4$. $F(000) = 944$. μ(Mo(Kα) radiation) = 0.68 cm^{-1}.

Intensities were converted to structure factors and normalized and the structure solved by direct methods using the MULTAN program package[9]. The origin defining reflections were 057, 710, 720, the enantiomorph 211, and additional reflections in the starting set 002 and 117. The E map resulting from the generated phases yielded the complete non-hydrogen skeleton of the molecule immediately upon inspection. Further computation was then carried out using the programs of the X-RAY 72 program system[10] adapted to the CYBER 73 computer at the University of Western Australia. The structure was refined by block-diagonal-least squares, the block parameters comprising the positional and thermal parameters of the skeleton atoms together with those of any associated hydrogen atoms. Non-hydrogen atom thermal motion was refined anisotropically according to the form:

$$\exp\ (-2\pi^2\ (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*))$$

All hydrogen atoms were successfully located in election density maps computed during the refinement procedure; with certain exceptions, the positional parameters were refined, with U(isotropic) being constrained to 0.10 Å^2. The exceptions noted are for certain methyl hydrogens: hydrogen atoms associated with C(24) were found to be disordered over two sets of mutually staggered sites and their positional parameters were determined from difference maps and included in the refinement constrained as invariants with population parameters of 0.5. Positional parameters of hydrogen attached to C(23) and C(28) could not be refined meaningfully and those were also located from difference maps and included as invariants in the refinement.

TABLE 1: ATOMIC FRACTIONAL CELL COORDINATES ($\times 10^3$, H; $\times 10^4$, OTHERS) AND THERMAL PARAMETERS ($\times 10^3$ Å^2) WITH LEAST SQUARES ESTIMATED STANDARD DEVIATIONS IN THE FINAL DIGIT IN PARENTHESES.

Non-hydrogen atoms

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	3132(5)	10820(7)	9928(11)	38(6)	59(7)	63(8)	0(6)	−7(6)	11(7)
C(2)	3752(6)	11596(8)	9952(13)	35(6)	71(9)	101(10)	−5(6)	15(8)	4(8)
C(3)	3499(6)	12454(7)	9223(11)	60(7)	68(8)	79(9)	−25(6)	−8(7)	−5(7)
O(3)	3936(4)	12822(6)	8436(8)	67(6)	134(7)	111(7)	−23(5)	15(5)	36(6)
C(4)	2713(5)	12857(7)	9451(10)	36(6)	61(7)	72(8)	−17(5)	−23(6)	4(7)
C(5)	2120(5)	11992(6)	9471(10)	41(6)	43(6)	58(7)	1(5)	−13(6)	9(6)
C(6)	1272(7)	12309(8)	9737(12)	41(6)	46(7)	100(12)	14(6)	−16(8)	7(8)
C(7)	0724(5)	11521(6)	9401(12)	39(6)	35(5)	75(8)	−13(6)	−31(7)	1(6)
C(8)	0872(5)	10554(6)	10108(9)	32(5)	45(6)	44(6)	3(5)	−4(5)	2(5)
C(9)	1752(5)	10307(7)	10028(9)	31(5)	46(6)	39(6)	10(5)	−16(5)	−6(6)
C(10)	2328(5)	11134(6)	10341(8)	41(6)	50(6)	44(6)	1(5)	−3(5)	−8(6)
C(11)	1912(6)	9371(8)	10726(12)	36(6)	56(7)	80(9)	−6(6)	3(7)	12(8)
C(12)	1432(6)	8535(9)	10227(10)	45(6)	59(7)	50(8)	−11(6)	−2(7)	13(7)
C(13)	0567(6)	8773(7)	10232(9)	48(6)	60(7)	31(6)	−2(5)	17(6)	−15(6)
C(14)	0392(5)	9717(6)	9499(8)	34(5)	51(6)	20(5)	2(5)	−4(5)	13(5)
C(15)	−0496(6)	9961(7)	9476(12)	42(6)	45(7)	77(10)	−6(6)	−15(7)	8(7)
C(16)	−1006(6)	9099(8)	9157(12)	52(7)	64(7)	66(8)	2(6)	−2(7)	−3(7)
C(17)	−0813(5)	8204(7)	9916(9)	58(6)	56(6)	44(7)	−16(6)	9(6)	−3(6)
C(18)	0046(6)	7962(6)	9746(9)	57(6)	39(6)	37(7)	−11(5)	8(6)	−19(5)
C(19)	0120(6)	6952(7)	10355(11)	80(8)	48(7)	54(8)	−7(6)	3(7)	13(6)
C(20)	0767(6)	6308(6)	9838(10)	94(8)	41(6)	56(7)	2(6)	11(7)	−17(6)
C(21)	−0687(7)	6470(3)	10081(11)	111(9)	43(6)	52(8)	−34(7)	−4(8)	1(6)
C(22)	−1208(7)	7286(8)	9472(12)	67(8)	60(7)	78(9)	−23(6)	0(8)	−14(8)
C(23)	2726(6)	13461(7)	10656(11)	67(7)	63(7)	93(9)	−18(7)	−2(7)	−21(8)
C(24)	2497(6)	13511(7)	8323(11)	68(8)	56(7)	104(9)	−22(7)	−32(8)	41(8)
C(25)	2360(7)	11345(8)	11769(11)	58(8)	44(8)	61(8)	10(6)	−11(7)	0(7)
C(26)	0600(11)	10743(11)	11502(13)	51(8)	70(9)	58(9)	12(8)	−8(8)	−4(7)
C(27)	0601(7)	9591(9)	8080(12)	55(7)	52(8)	51(8)	−8(7)	2(7)	16(6)
C(28)	−1032(6)	8761(7)	11351(10)	62(7)	68(7)	71(9)	−16(6)	18(7)	1(7)
C(29)	1032(9)	6356(8)	8644(13)	120(12)	49(8)	78(11)	−6(8)	5(10)	−7(7)
C(30)	1009(10)	5557(10)	10721(14)	233(18)	118(12)	123(13)	127(13)	35(14)	44(11)

Hydrogen atoms; the final column gives r_{C-H}(Å)

H(1a)	336(6)	1028(7)	1046(10)	100(−)	1.0(1)
H(1b)	316(6)	1054(7)	890(10)	100(−)	1.2(1)
H(2a)	376(6)	1199(7)	1093(10)	100(−)	1.2(1)
H(2b)	421(6)	1130(7)	970(10)	100(−)	0.9(1)
H(5)	208(5)	1167(7)	846(9)	100(−)	1.2(1)
H(6a)	123(7)	1247(8)	1055(11)	100(−)	0.9(1)
H(6b)	111(6)	1290(7)	942(11)	100(−)	0.9(1)
H(7a)	025(6)	1161(8)	960(11)	100(−)	0.9(1)
H(7b)	078(5)	1126(6)	821(10)	100(−)	1.3(1)
H(9)	182(5)	1016(7)	985(10)	100(−)	1.2(1)
H(11a)	172(6)	937(7)	1166(10)	100(−)	1.0(1)
H(11b)	256(6)	936(6)	1064(9)	100(−)	1.1(1)
H(12a)	146(6)	805(7)	1078(10)	100(−)	0.9(1)
H(12b)	154(6)	850(8)	943(10)	100(−)	0.8(1)
H(13)	052(6)	884(7)	111(10)	100(−)	0.9(1)
H(15a)	−075(6)	1028(7)	1027(11)	100(−)	1.1(1)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
H(15b)	−054(7)	1040(8)	891(11)	100(−)	0.9(1)				
H(16a)	−163(6)	941(7)	930(10)	100(−)	1.2(1)				
H(16b)	−088(6)	892(7)	813(10)	100(−)	1.1(1)				
H(18)	018(5)	785(7)	873(10)	100(−)	1.1(1)				
H(19)	022(6)	699(7)	1144(10)	100(−)	1.2(1)				
H(24)	−064(6)	580(7)	943(9)	100(−)	1.2(1)				
H(21b)	−089(5)	609(7)	1102(10)	100(−)	1.2(1)				
H(22a)	−182(6)	716(7)	978(10)	100(−)	1.1(1)				
H(22b)	−114(6)	720(7)	847(10)	100(−)	1.1(1)				
H(23a)	212(−)	1402(−)	891(−)	100(−)	1.3(−)				
H(23b)	283(−)	1409(−)	800(−)	100(−)	1.0(−)				
H(23c)	202(−)	1314(−)	797(−)	100(−)	1.0(−)				
H(24a)	212(−)	1391(−)	1094(−)	100(−)	1.3(−)				
	198(−)	1357(−)	1068(−)	100(−)	1.3(−)				
H(24b)	337(−)	1343(−)	1103(−)	100(−)	1.2(−)				
	308(−)	1406(−)	1081(−)	100(−)	1.0(−)				
H(24c)	237(−)	1329(−)	1147(−)	100(−)	1.1(−)				
	288(−)	1286(−)	1156(−)	100(−)	1.3(−)				
H(25a)	191(6)	1175(8)	1206(10)	100(−)	1.0(−)				
H(25b)	243(6)	1065(7)	1219(9)	100(−)	1.1(1)				
H(25c)	265(6)	1183(8)	1202(11)	100(−)	0.9(1)				
H(26c)	084(6)	1015(7)	1205(10)	100(−)	1.1(+)				
H(26b)	078(6)	1127(7)	1192(11)	100(−)	0.9(+)				
H(26c)	017(6)	1064(8)	1145(12)	100(−)	0.8(1)				
H(27a)	030(6)	891(7)	761(10)	100(−)	1.2(1)				
H(27b)	061(7)	1006(7)	770(11)	100(−)	0.8(1)				
H(27c)	110(6)	944(8)	806(11)	100(−)	0.9(1)				
H(28a)	−067(−)	914(−)	1109(−)	100(−)	1.3(−)				
H(28b)	−160(−)	849(−)	1138(−)	100(−)	1.0(−)				
H(28c)	−087(−)	763(−)	1206(−)	100(−)	1.3(−)				
H(29a)	090(7)	680(8)	813(11)	100(−)	0.9(1)				
H(28b)	149(6)	577(7)	836(10)	100(−)	1.2(1)				

H(24a), H(24b), H(24c): populations 0.5

TABLE II: Interatomic distances and angles (Å, deg.) (non-hydrogen atoms only) with least squares estimated standard deviations in the final digit in parentheses.

C(1) – C(2)	1.53(1)	C(11) – C(12)	1.53(2)
C(1) – C(10)	1.52(1)	C(12) – C(13)	1.53(1)
C(2) – C(3)	1.49(2)	C(13) – C(18)	1.54(1)
C(3) – O(3)	1.24(1)	C(13) – C(14)	1.56(1)
C(3) – C(4)	1.49(1)	C(14) – C(27)	1.56(1)
C(4) – C(23)	1.55(1)	C(14) – C(15)	1.57(1)
C(4) – C(24)	1.53(2)	C(15) – C(16)	1.53(1)
C(4) – C(5)	1.59(1)	C(16) – C(17)	1.53(1)
C(5) – C(6)	1.56(1)	C(17) – C(22)	1.53(1)
C(5) – C(10)	1.56(1)	C(17) – C(28)	1.58(1)
C(6) – C(7)	1.50(1)	C(17) – C(18)	1.54(1)
C(7) – C(8)	1.57(1)	C(18) – C(19)	1.56(1)
C(8) – C(9)	1.57(1)	C(19) – C(21)	1.58(2)
C(8) – C(14)	1.58(1)	C(21) – C(22)	1.59(2)
C(8) – C(26)	1.57(1)	C(19) – C(20)	1.54(1)
C(9) – C(10)	1.56(1)	C(20) – C(29)	1.35(2)
C(10) – C(25)	1.54(1)	C(20) – C(30)	1.47(2)
C(9) – C(11)	1.53(1)		

C(10) – C(1) – C(2)	115.6(9)	C(9) – C(11) – C(12)	112.9(9)
C(1) – C(2) – C(3)	111.0(9)	C(11) – C(12) – C(13)	111.3(9)
C(2) – C(3) – C(4)	119.1(9)	C(12) – C(13) – C(14)	111.8(8)
C(2) – C(3) – O(3)	120.3(9)	C(14) – C(13) – C(18)	110.1(8)
O(3) – C(3) – C(4)	120.6(9)	C(12) – C(13) – C(18)	114.3(9)
C(3) – C(4) – C(23)	109.6(8)	C(13) – C(14) – C(8)	108.8(7)
C(3) – C(4) – C(24)	109.3(8)	C(13) – C(14) – C(27)	109.8(8)
C(3) – C(4) – C(5)	107.7(8)	C(13) – C(14) – C(15)	112.4(7)
C(23) – C(4) – C(24)	108.6(8)	C(8) – C(14) – C(27)	110.9(8)
C(23) – C(4) – C(5)	107.7(8)	C(8) – C(14) – C(15)	111.1(7)
C(24) – C(4) – C(5)	114.8(8)	C(27) – C(14) – C(15)	103.7(8)
C(4) – C(5) – C(6)	113.2(8)	C(14) – C(15) – C(16)	113.3(8)
C(4) – C(5) – C(10)	116.5(8)	C(15) – C(16) – C(17)	113.8(9)
C(6) – C(5) – C(10)	109.2(8)	C(16) – C(17) – C(18)	109.3(8)
C(5) – C(6) – C(7)	110.0(9)	C(16) – C(17) – C(22)	115.4(9)
C(6) – C(7) – C(8)	114.8(9)	C(16) – C(17) – C(28)	109.9(8)
C(7) – C(8) – C(9)	108.9(7)	C(28) – C(17) – C(18)	112.1(8)
C(7) – C(8) – C(14)	111.1(7)	C(28) – C(17) – C(22)	107.8(8)
C(7) – C(8) – C(26)	104.8(8)	C(22) – C(17) – C(18)	102.2(8)
C(26) – C(8) – C(14)	110.6(7)	C(17) – C(18) – C(13)	111.4(8)
C(26) – C(8) – C(9)	112.3(8)	C(17) – C(18) – C(19)	103.4(8)
C(9) – C(8) – C(14)	109.1(7)	C(13) – C(18) – C(19)	118.8(8)
C(8) – C(9) – C(10)	116.5(7)	C(18) – C(19) – C(20)	116.3(9)
C(8) – C(9) – C(11)	109.8(7)	C(18) – C(19) – C(21)	103.8(8)
C(10) – C(9) – C(11)	114.6(8)	C(20) – C(19) – C(21)	109.2(8)
C(9) – C(10) – C(1)	107.9(7)	C(19) – C(21) – C(22)	105.6(8)
C(9) – C(10) – C(5)	107.3(7)	C(21) – C(22) – C(17)	103.0(9)
C(9) – C(10) – C(25)	111.9(8)	C(19) – C(20) – C(29)	123.6(9)
C(25) – C(10) – C(1)	107.7(9)	C(19) – C(20) – C(30)	113.6(9)
C(25) – C(10) – C(5)	116.3(8)	C(19) – C(20) – C(30)	122.5(10)
C(1) – C(10) – C(5)	105.2(8)		

TABLE III: Torsion angles (deg.) within the non-hydrogen skeleton, together with the corresponding values for methyl melaleucate iodoacetate, and 3β-Acetoxy-20-hydroxylupane.

C(10)–C(1) –C(2) –C(3)	– 52.8,	– 56.5, – 57.0
C(1) –C(2) –C(3) –O(3)	–131.5,	176.8, 176.8
C(1) –C(2) –C(3) –C(4)	47.9,	62.6, 55.1
C(2) –C(3) –C(4) –C(23)	–162.1,	–170.2, –167.1
C(2) –C(3) –C(4) –C(24)	79.4,	64.9, 73.8
C(2) –C(3) –C(4) –C(5)	– 45.7,	– 53.1, – 49.8
O(3) –C(3) –C(4) –C(23)	–101.1,	71.6, 69.2
O(3) –C(3) –C(4) –C(24)	– 17.3,	– 53.3, – 49.9
O(3) –C(3) –C(4) –C(5)	133.8,	171.3, –173.4
C(3) –C(4) –C(5) –C(10)	50.2,	46.5, 51.1
C(23)–C(4) –C(5) –C(6)	– 64.6,	– 56.6, – 61.4
C(3) –C(4) –C(4) –C(6)	178.5,	–175.7, –178.0
C(24)–C(4) –C(5) –C(6)	56.8,	61.9, 61.7
C(23)–C(4) –C(5) –C(10)	167.3,	165.6, 167.8
C(24)–C(4) –C(5) –C(10)	– 71.5,	– 75.9, – 69.1
C(4) –C(5) –C(6) –C(7)	164.5,	158.6, 160.0
C(10)–C(5) –C(6) –C(7)	– 63.5,	– 60.1, – 64.4
C(4) –C(5) –C(10)–C(1)	– 55.0,	– 47.3, – 53.1
C(6) –C(5) –C(10)–C(1)	174.8,	173.8, 175.2
C(4) –C(5) –C(10)–C(9)	–170.0,	–168.6, –168.8
C(6) –C(5) –C(10)–C(9)	59.8,	52.5, 59.4
C(4) –C(5) –C(10)–C(25)	63.7,	66.4, 63.4
C(5) –C(6) –C(7) –C(8)	57.7,	58.1, 58.7
C(6) –C(7) –C(8) –C(9)	– 47.9,	– 50.4, – 50.8
C(6) –C(7) –C(8) –C(14)	–168.2,	–170.3, –170.7
C(6) –C(7) –C(8) –C(26)	72.2,	74.1, 70.2
C(7) –C(8) –C(9) –C(10)	46.9,	48.0, 51.0
C(7) –C(8) –C(9) –C(11)	179.5,	–178.3, –179.7
C(26)–C(8) –C(9) –C(10)	– 68.6,	– 72.5, – 68.4
C(26)–C(8) –C(9) –C(11)	64.0,	61.3, 60.8
C(14)–C(8) –C(9) –C(10)	168.4,	168.0, 169.8
C(14)–C(8) –C(9) –C(11)	– 59.0,	– 58.3, – 60.9
C(7) –C(8) –C(14)–C(15)	– 56.1,	– 63.0, – 59.2
C(9) –C(8) –C(14)–C(19)	–176.2,	–176.1, –177.9
C(26)–C(8) –C(14)–C(15)	59.9,	52.5, 59.4
C(7) –C(8) –C(14)–C(13)	179.4,	175.3, 179.3
C(9) –C(8) –C(14)–C(13)	59.3,	54.4, 60.6
C(26)–C(8) –C(14)–C(13)	– 64.6,	– 69.2, – 62.1
C(7) –C(8) –C(14)–C(27)	58.9,	51.8, 58.0
C(9) –C(8) –C(14)–C(27)	– 61.3,	– 69.2, – 60.8
C(26)–C(8) –C(14)–C(27)	174.9,	167.2, 176.5
C(8) –C(14)–C(13)–C(12)	– 57.4,	– 52.4, – 59.4
C(15)–C(14)–C(13)–C(12)	178.8,	–175.8, 178.8
C(27)–C(14)–C(13)–C(12)	63.8,	68.4, 62.1
C(8) –C(14)–C(13)–C(18)	174.5,	–178.6, 169.0
C(15)–C(14)–C(13)–C(18)	50.7,	57.9, 47.1
C(27)–C(14)–C(13)–C(18)	– 64.3,	– 57.9, – 69.5
C(8) –C(14)–C(15)–C(16)	–167.7,	–175.9, –162.6
C(13)–C(14)–C(15)–C(16)	– 45.2,	– 53.9, – 43.4
C(27)–C(14)–C(15)–C(16)	73.2,	67.1, 76.7
C(14)–C(15)–C(16)–C(17)	47.9,	50.2, 49.7
C(16)–C(17)–C(18)–C(13)	61.5,	61.8, 66.3
C(22)–C(17)–C(18)–C(13)	–175.9,	–173.7, –170.5
C(28)–C(17)–C(18)–C(13)	– 60.8,	– 58.1, – 56.5
C(16)–C(17)–C(18)–C(19)	–169.9,	–169.0, –158.3
C(22)–C(17)–C(18)–C(19)	– 47.3,	– 44.5, – 35.1
C(28)–C(17)–C(18)–C(19)	67.8,	71.1, 78.9
C(15)–C(16)–C(17)–C(18)	– 55.2.	– 52.8, – 59.2
C(15)–C(16)–C(17)–C(22)	–169.7,	–167.0, –172.8
C(15)–C(16)–C(17)–C(28)	68.4,	72.1, 64.2
C(16)–C(17)–C(22)–C(21)	160.7,	160.5, 164.0
C(18)–C(17)–C(22)–C(21)	42.1,	40.8, 46.6
C(28)–C(17)–C(22)–C(21)	– 76.3,	– 79.7, – 71.0
C(17)–C(22)–C(21)–C(19)	– 21.6,	– 22.1, – 41.4
C(22)–C(21)–C(19)–C(18)	– 6.7,	– 6.1, 18.2
C(22)–C(21)–C(19)–C(20)	–131.1,	–134.6, –108.2
C(21)–C(19)–C(20)–C(29)	87.5,	– 81.0, 158.6
C(21)–C(19)–C(20)–C(30)	– 85.5,	94.2, – 64.5
C(18)–C(19)–C(20)–C(29)	– 29.4,	162.0, 43.0
C(18)–C(19)–C(20)–C(30)	157.6,	– 22.8, 180.0
C(17)–C(18)–C(19)–C(20)	152.6,	152.1, 132.6
C(13)–C(18)–C(19)–C(20)	– 83.6,	– 84.9, – 98.2
C(17)–C(8) –C(19)–C(21)	32.7,	30.8, 10.0
C(13)–C(18)–C(19)–C(21)	156.5,	153.8, 139.2
C(12)–C(13)–C(18)–C(17)	173.5,	169.0, 170.8
C(12)–C(13)–C(18)–C(19)	53.8,	49.2, 42.5
C(14)–C(13)–C(18)–C(17)	– 59.7,	– 64.3, – 60.4
C(14)–C(13)–C(18)–C(19)	–179.4,	175.9, 171.2
C(11)–C(12)–C(13)–C(14)	54.3,	54.1, 59.9
C(11)–C(12)–C(13)–C(18)	–179.9,	177.9, –171.4
C(9) –C(11)–C(12)–C(13)	– 54.1,	– 56.9, – 57.6
C(8) –C(9) –C(11)–C(12)	56.7,	61.1, 58.6
C(10)–C(9) –C(11)–C(12)	–169.7,	–162.7, –168.6
C(8) –C(9) –C(10)–C(1)	–167.4,	–166.3, –170.1
C(11)–C(9) –C(10)–C(1)	62.1,	61.5, 61.6
C(8) –C(9) –C(10)–C(5)	– 54.3,	– 48.5, – 56.2
C(8) –C(9) –C(10)–C(25)	74.4,	71.1, 73.5
C(11)–C(9) –C(10)–C(5)	175.3,	179.3, 175.5
C(11)–C(9) –C(10)–C(25)	– 56.0,	– 61.1, – 54.8
C(2) –C(1) –C(10)–C(5)	55.3,	48.8, 52.5
C(2) –C(1) –C(10)–C(9)	169.9,	166.5, 165.7
C(2) –C(1) –C(10)–C(25)	– 69.1,	– 65.6, – 72.3

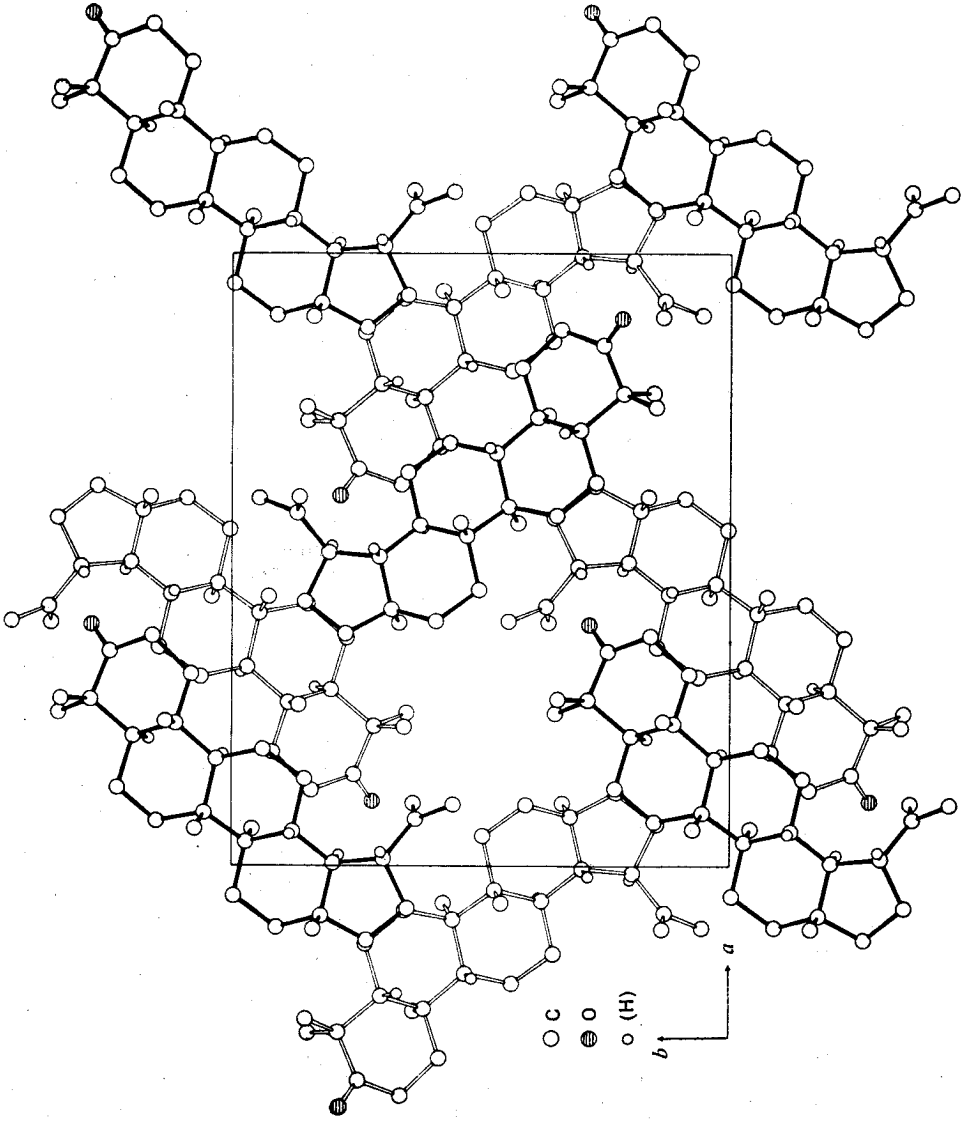


Fig. 1. Unit cell contents projected down *c*

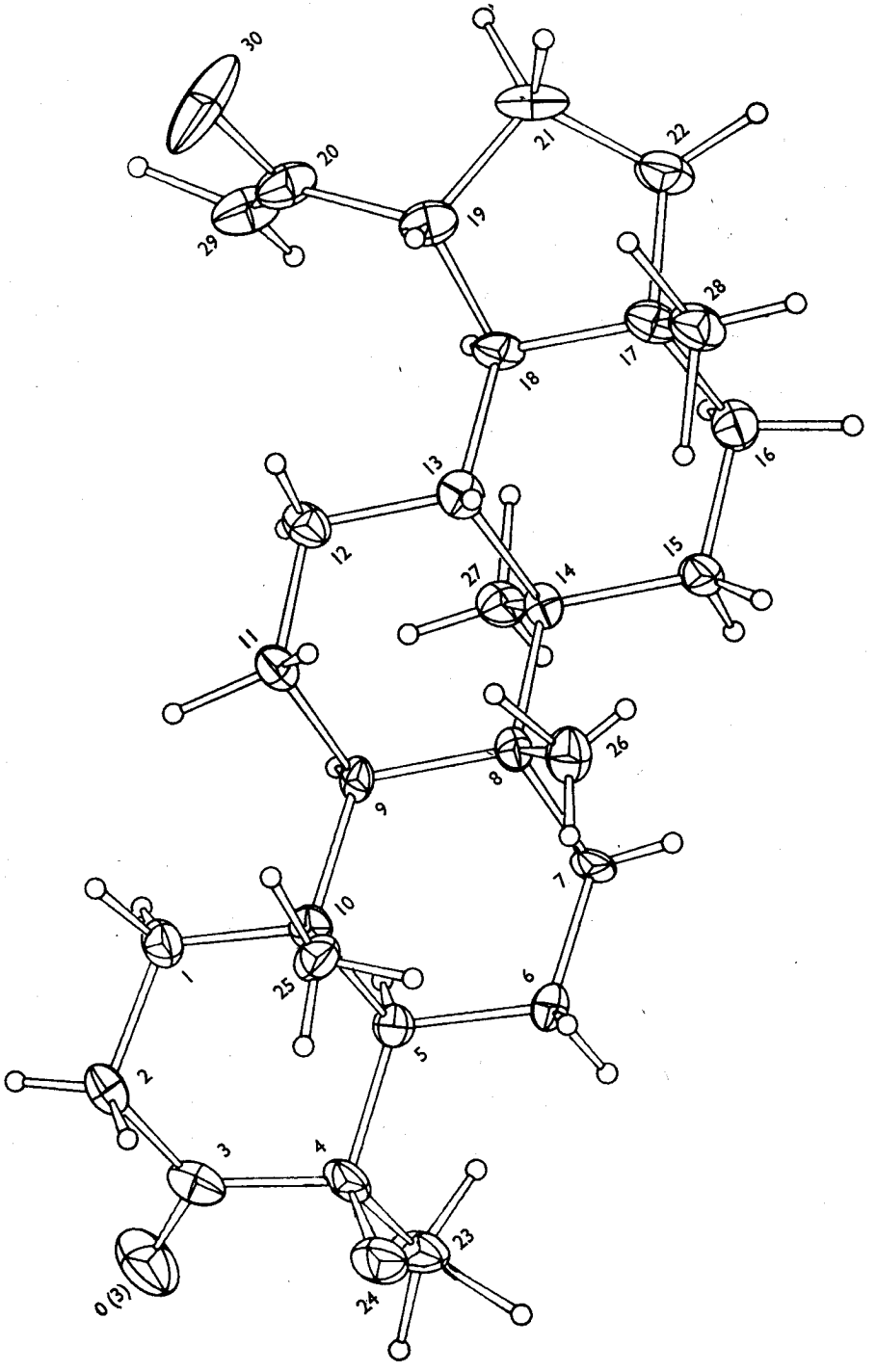


Fig. 2. Molecular projection showing 20% thermal ellipsoids and atom labelling. Hydrogen atoms are shown with an arbitrary radius of 0.1Å.

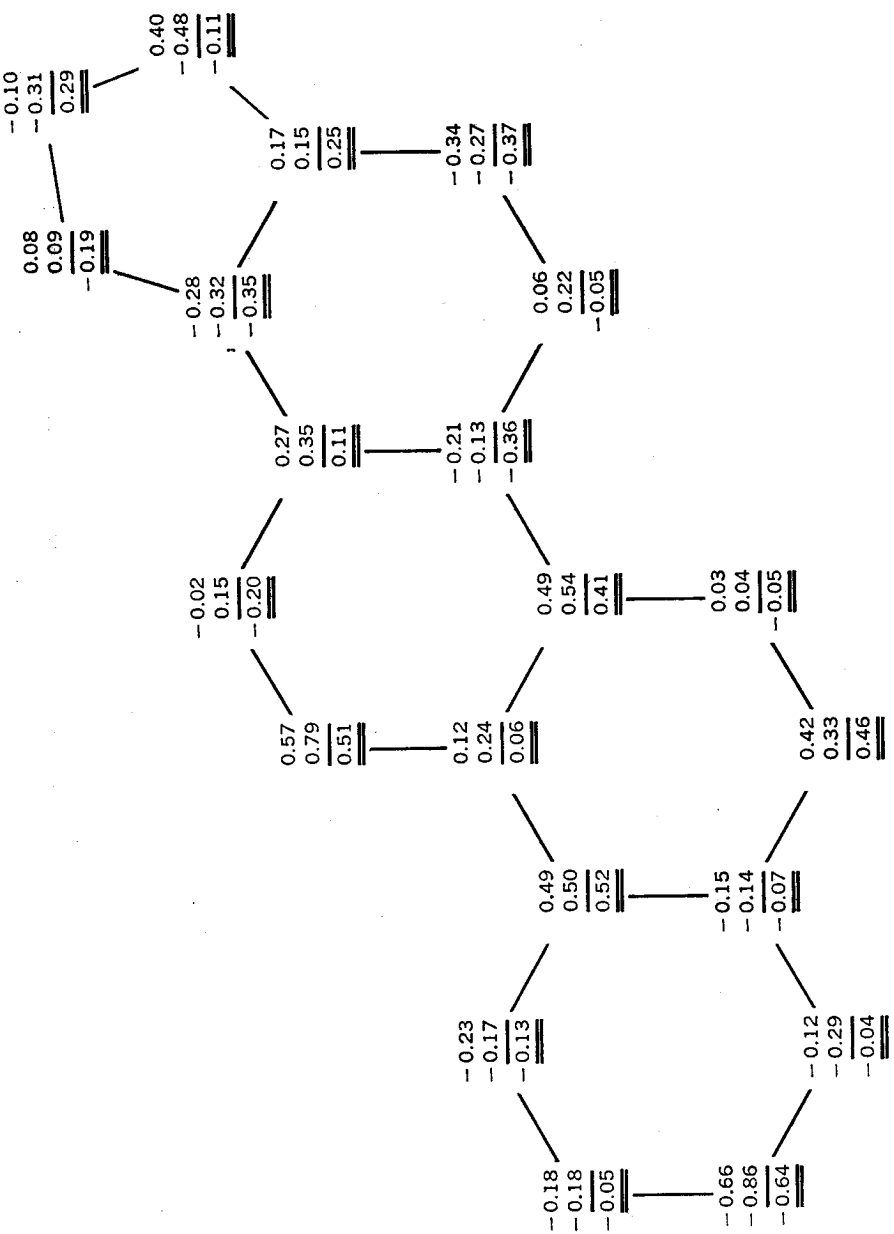


Fig. 3. Deviations from the least squares plane through the ring system skeleton for (i) lup-20(29)-ene-3-one (ii) melaleucic acid iodoacetate (italics) (iii) 3β-acetoxy-20-hydroxylupane (bold type).

No hydrogen atoms at all could be located about C(30); these appeared to be totally disordered and were omitted from the refinement. Refinement converged with all parameter shifts $< 0.2\sigma$ the residuals being:

$$R = \Sigma| |F_o| - |F_c| |/\Sigma|F_o| = 0.075$$
$$R' = (\Sigma w| |F_o| - |F_c| |^2/\Sigma w|F_o|^2)^{1/2} = 0.079$$

In the final stages of refinement weights w given by

$$w = (\sigma^2(F_o) + n \times 10^{-4}(F_o)^2)^{-1}$$

were assigned to the data to equalize $w.\Delta F_o^2$ over the data set; the optimum value of n was found to be 5. (During the latter stages of refinement the function minimized was $\Sigma w| |F_o| - |F_c| |^2$).

Neutral atom scattering factors were employed throughout, those for C and O being corrected for the anomalous dispersion components ($\Delta f'$, $\Delta f''$)[11-13].

Numbering of the carbon skeleton is systematic and follows the scheme in the molecular diagram of Fig. 2. Hydrogen and oxygen atoms are numbered according to the carbon atom to which they are attached; these are suffixed a, b, c where it is necessary to distinguish between them. Results are tabulated in Tables I (atom parameters), II(molecular geometry) and III(torsion angles). Tables of structure amplitudes are deposited with the Editor; copies may be obtained on application.

The crystal lattice of (4) contains discrete molecules with no unusually short intermolecular contacts. The skeleton is identical with that previously observed in (2)[5] and (3)[6]. The conformation is very similar with only minor significant variations in geometry, primarily as a result of variations in the peripheral substituents, and a change in conformation of the five-membered ring, probably a consequence of "packing forces" (Fig. 3, Table III). The parity of the configuration described, although given as the same for all three compounds, has only been directly established crystallographically on an absolute basis for (2)[5].

Acknowledgement

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บทคัดย่อ

บทความนี้บรรยายถึงการวิจัยหาส่วนประกอบทางเคมีของต้นเสลดพังพอน [*Clinacanthus nutans* (Burn) Lindau (*C. Siamensis* Bremek)] และการหา structure ของ Lup-20(29)-ene-3-one โดยวิธี X-ray diffraction