Novel α-Methyldeoxybenzoins from the Heartwood of *Pterocarpus angolensis* D.C.: Absolute Configuration and Conformation of the First Sesquiterpenylangolensis, and *X*-Ray Crystal Structure of 4-*O*-α-Cadinyl-angolensin

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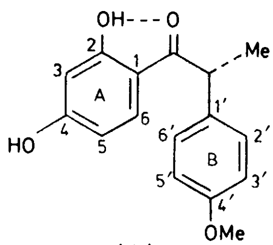
The known 2,4-dihydroxy-4′-methoxy-α-methyldeoxybenzoin, (α*R*)-angolensin, is accompanied by the novel (α*S*)-4-*O*-methylangolensin and a unique epimeric pair comprising (α*R*,1″*R*,4″*S*,4″a*R*,8″a*R*)-4-*O*-α-cadinylangolensin and (α*R*,1″*S*,4″*S*,4″a*R*,8″a*R*)-4-*O*-*T*-cadinylangolensin in the heartwood of *Pterocarpus angolensis* D.C. The absolute configuration and conformation of the former was determined by *X*-ray analysis.
Bis-(2-ethylhexyl) phthalate accompanies the above metabolites.

ALTHOUGH the wood of *P. angolensis* (muninga, kiaat), known for its remarkable durability,[1] has over the years been the subject of a series of investigations,[2-7] the from the biochemical viewpoint, was first obtained as a racemate by King *et al.*,[3] and its absolute configuration established as (α*R*) by Ollis *et al.*[8] Its natural distri-



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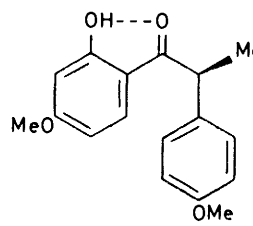

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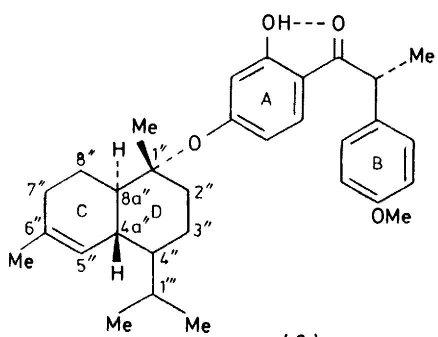

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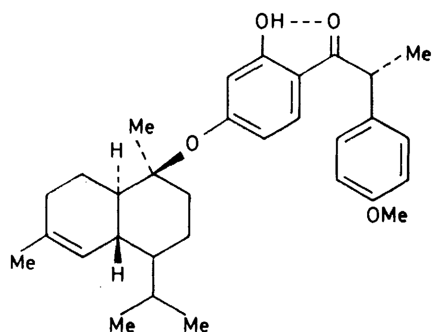

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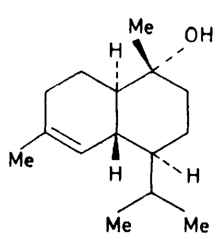

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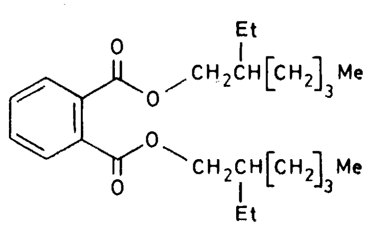


(6)

range of flavonoid-type compounds isolated from it was confined mainly to the isoflavonoids prunetin, muningin, and 7-methyltectoriginin accompanied by angolensin (1), a 2,4-dihydroxy-4′-methoxy-α-methyldeoxybenzoin. The latter, a simple flavonoid of exceptional structure bution has hitherto been confined to *Pterocarpus*[2-7] and *Pericopsis*[9] species. The present more exhaustive re-examination of *Pterocarpus angolensis* has extended the range of natural α-methyldeoxybenzoins to (α*S*)-4-*O*-methylangolensin (2) and the unique epimeric pair of 4-*O*-sesquiterpenyl derivatives, (α*R*)-4-*O*-α-cadinylangolensin (3) and (αR)-4-*O*-*T*-cadinylangolensin (4).*

Considering the total absence of ^1H n.m.r. data, the basic α-methyldeoxybenzoin skeletal structure of angolensin (1), and of its enantiomeric 4-*O*-methyl *analogue* (2), may be recognized from the typical A_3X-system (quartet, δ 4.57 and 4.53 respectively and a doublet, δ 1.47) associated with the vicinal methyl–methine coupling in the α-position. Attachment of this unit to the A-ring *via* a carbonyl group is illustrated by the presence of a hydrogen-bonded hydroxy-group in both cases (δ 7.00 and 9.66) respectively), and substantiated by low-frequency carbonyl i.r. absorption ($\nu_{max.}$ 1 640 cm^{-1}). Assignment of further substituents to C-4 of the A-rings is in line with the observed aromatic ABX-systems with low-field *ortho*-coupled doublets (δ 7.63) allocated to the C-6 proton, while the remainder of the aromatic region, displaying an AA′BB′-system, is assigned to the *para*-substituted B-ring. Conclusive evidence from mass spectral fragmentation, based on the expected α-cleavage of the carbonyl group, indicates the B-ring as the location of the methoxy-group in angolensin (1) [*m/e* 137 (100%) and 135 (79)], while both A- and B-rings possess a single methoxy-function in the 4-*O*-methyl analogue [*m/e* 151 (100%) and 135 (54)]. Both structures, $C_{16}H_{16}O_4$ and $C_{17}H_{18}O_4$, respectively, are confirmed by elemental analysis.

Comparison of c.d. spectra obtained from (α*R*)-angolensin [8,10] (1) and 4-*O*-methylangolensin (2) shows identical but inverted Cotton effects. This unambiguously illustrates the α*S*-configuration of 4-*O*-methylangolensin (2) and thus defines the first α-methyldeoxybenzoin from natural sources with this configuration.

Mass fragmentation and ^1H n.m.r. spectra of 4-*O*-cadinylangolensin (3) clearly display all the elements of a basic C_{15}-structure identical to that of angolensin (1), apart from the absence of the 4-OH proton resonance. This is replaced by a broadened low-field singlet (δ 5.44) and considerable absorption to high field (*ca.* δ 0.7—2.3), all of which integrate for 25 additional protons. Similar comparison of ^{13}C n.m.r. data indicates a complement of 15 carbons for the derivative (3) relative to (1), thus correlating with angolensin coupled to a $C_{15}H_{25}$ unit. Corroborative evidence for this structure stems from mass spectral fragmentation yielding *m/e* 341 (2.1%) and 135 (91) by α-cleavage, as well as *m/e* 206 (22%) and 272 (47) corresponding to $C_{15}H_{26}$ and angolensin respectively, presuming H-transfer for both fragments. The molecular ion, M^+ *m/e* 476, comprising these units was obtained by field desorption mass spectrometry. The resulting molecular formula, $C_{31}H_{40}O_4$ is confirmed by elemental analysis.

Comparison of ^1H n.m.r. data of (3) (Table 1) with spectra of several sesquiterpenoids immediately discloses the nature of the $C_{15}H_{25}$ unit, with the appropriate peaks very similar to those obtained from (—)-α-cadinol [11-13] (β-ol, 5), isolated from Javanese citronella oil. Despite the complexity of the high-field region the four associated methyls are readily discernible, with the vinylic 6″-CH_3 strongly deshielded (broadened singlet, δ 1.67), 1″-CH_3 as a sharp deshielded singlet (δ 1.27), and the non-equivalent 4-isopropyl methyl

TABLE 1

^1H and ^{13}C n.m.r. chemical shifts (δ) [a] of (α*R*)-angolensin (1), (α*S*)-4-*O*-methylangolensin (2), (α*R*)-4-*O*-α-cadinylangolensin (3), (α*R*)-4-*O*-*T*-cadinylangolensin (4), and α-cadinol (5) [b]

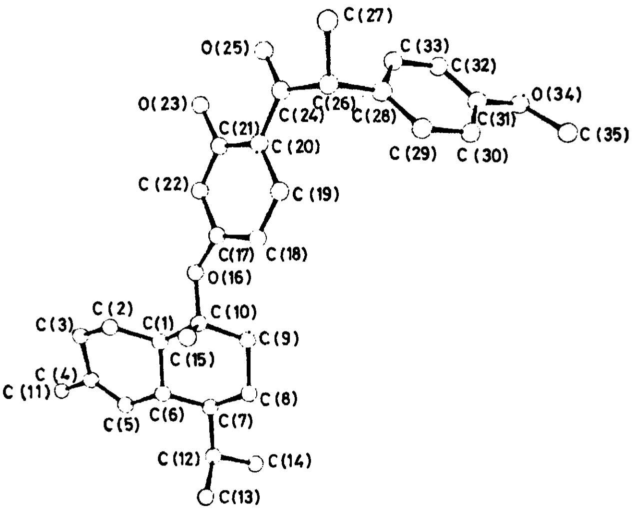
	^1H				
	(1)	(2)	(3)	(4)	(5)
3-H	6.30d	6.31d	6.47d	6.44d	
5-H	6.23dd	6.28dd	6.34dd	6.28dd	
6-H	7.63d	7.63d	7.61d	7.56d	
2′-H	7.17d	7.13d	7.19d	7.13d	
3′-H	6.77d	6.75d	6.80d	6.75d	
5′-H	6.77d	6.75d	6.80d	6.75d	
6′-H	7.17d	7.13d	7.19d	7.13d	
α-H	4.57q	4.53q	4.56q	4.53q	
2-OH	13.00s	9.66s	9.91s	9.63s	
4-OH	6.70s				
4-OMe		3.69s			
4′-OMe	3.73s	3.75s	3.72s	3.72s	
α-Me	1.47s	1.47d	1.47d	1.48d	
5″-H			5.44br,s	5.31br,s	5.43br,s
1″-Me			1.27s	1.41s	1.08s
6″-Me			1.67br,s	1.66br,s	1.63br,s
4″-CHMe			0.89d	0.88d	0.89d
4″-CHMe			0.75d	0.73d	0.73d

	^{13}C		
	(1)	(3)	(5)
1-C	111.3	112.5	
2-C	161.3	161.3	
3-C	102.5	108.4	
4-C	164.4	163.1	
5-C	106.3	112.5	
6-C	131.3	129.4	
α-C	45.0	44.7	
CO	203.8	203.1	
α-Me	18.1	19.3	
1′-C	132.5	132.2	
2′-C	126.9	126.9	
3′-C	113.1	113.1	
4′-C	156.9	156.8	
5′-C	113.1	113.1	
6′-C	126.9	126.9	
4′-OMe	54.1	53.8	
1″-C		83.0	70.0
5″-C		120.6	119.1
6″-C		133.4	131.3
1″-Me		23.8	22.2
6″-Me		25.6	24.5
4″-CHMe		18.8	19.5
4″-CHMe		15.0	13.9

[a] Relative to Me_4Si. [b] ^1H and ^{13}C chemical shifts corresponding to the 1‴, 2″, 3″, 4″, 4a″, 7″, 8″, and 8a″ positions fall into the ranges 1.59—2.63m (3), 1.00—2.55m (4), 1.00—2.45m (5) and 21.2—48.0 (3), 20.0—45.0 (5), respectively.

* Naphthalene-type numbering is used for the cadinol unit; *Chemical Abstracts* uses terpenoid numbering for cadinane and its derivatives.

groups (asymmetric centre) appearing as doublets (J 6.88 Hz, δ 0.75 and 0.89). Splitting patterns of the latter were confirmed by decoupling of the multiplet at δ 2.17 (isopropyl methine) which causes their collapse to singlets. ^{13}C Off-resonance (single-frequency off-resonance decoupling) n.m.r. spectra (Table 1) confirm the presence of four methyl groups [δ 15.0 and 18.8 (both q, isopropyl methyl), 23.8 (q, 1″-CH_3), and 25.6 (q, 6″-CH_3) p.p.m.] in addition to the α-methyl [δ 19.1 (q) p.p.m.] of angolensin. The vinyl proton, H-5″, is deshielded to low field (δ 5.44) as a broadened singlet indicative of a 1,6-*trans* ring juncture.[14] Owing to the complexity of inter-proton coupling and signal overlap exhibited by the sesquiterpenoid portion of the molecule even at 360 MHz, unambiguous interpretation of the remaining methylene and methine protons is not possible.



X-Ray crystal structure of (α*R*)-4-*O*-α-cadinylangolensin (3) showing the crystallographic numbering system

Final confirmation of the structure, determination of the absolute configuration at the point of juncture, C-1″, and also analysis of the conformation is, however, given by *X*-ray analysis.

For the *X*-ray structure determination the atomic numbering scheme for the molecule as shown in the Figure was used; this is unrelated to the chemical system which proved inadequate. The structure was determined by direct methods and refined by full-matrix least squares, resulting in a final R value of 0.084. All non-hydrogen atoms were refined anisotropically and 25 could be located. Final calculations were based on the calculated positions of 39 hydrogen atoms, the position of H-23 (2-OH) being obtained by a difference-Fourier map. Existence of the intramolecular hydrogen bonding associated with the latter is clearly confirmed by the O(23)–H(23) bond length (0.927 Å) accompanied by an O(25)–H(23) distance of 1.768 Å. All the remaining bond lengths and angles are as expected and indicate the composition of the molecule as an α-methyldeoxybenzoin (angolensin) of known absolute configuration, R,[8,10] attached to a sesquiterpenoid, α-cadinol, with a 1,6-*trans* (4″a,8″-a-*trans*) ring junction. The absolute configuration of the molecule is thus 1*R*,6*R*,7*S*,10*R*,26*R*) (numbering as in Figure) [α*R*,1″*R*,4″*S*,4″a*R*,8″a*R*″) numbered as in (3)].

Conformations of the non-aromatic six-membered rings C [C(1)—C(6)] and D [C(1), C(6)—C(10)] were analysed in terms of puckering parameters as defined by Boeyens.[15] These parameters (Table 2) suggest a chair conformation

TABLE 2

Puckering parameters for rings C and D

Ring	Atoms	θ	φ	Q	Symbolic description[a]
C	C(1), C(2), C(3), C(4), C(5), C(6)	128.8	154.1	0.51	$^2S_1 \sim {}^2H_1$
D	C(1), C(6), C(7), C(8), C(9), C(10)	4.1	137.5	0.55	$^{10}C_7$

[a] Ref. 15.

for ring D while the C-ring exhibits intermediate half-chair and screw-boat character, approximating most likely to a sofa conformation.

4-*O*-*T*-Cadinylangolensin (4), a non-crystalline di-astereoisomer, was found to be virtually identical to 4-*O*-α-cadinyl angolensin (3) with regard to mass spectrometry, ^{1}H n.m.r., and c.d. Their difference is confined to minor variations in the appearance of the c.d. curves in the region 280—360 nm, in conjunction with a downfield shift (Δδ 0.14) of the 1″-CH_3 in the ^{1}H n.m.r. spectrum of the former (4). This indicates a C-1″ epimeric relationship. The sesquiterpene unit is thus likely to possess the same absolute configuration as *T*-cadinol (α-ol),[16] with an unstable *axial* arrangement of the angolensin unit (*cf.* Figure). This may account for the low natural abundance of (4) relative to (3). These compounds may accordingly be fully designated as (α*R*,1″*S*,4″*S*,4″a*R*,8″a*R*)- and (α*R*,1″*R*,4″*S*,4″a*R*,8″a*R*)-2-hydroxy-4′-methoxy-4-[1″,2″,3″,4″,4″a,7″,8″,8″a-octahydro-1″,6″-dimethyl-4″-(1‴-methylethyl)-1″-naphthyloxy]-α-methyldeoxybenzoin [(4) and (3) respectively]. The function of the biochemically introduced sesquiterpenyl units is speculatively considered as conferring solubility on the C_{15}-angolensin in lipids present in the walls of the individual cells of the wood, such localization thus enhancing the efficiency of the flavonoid as an anti-fungal agent.

The sesquiterpenylangolensin pair are accompanied in the non-polar fraction of the n-hexane extract by a colourless oil, identified as bis-(2-ethylhexyl) phthalate (6). The ^{1}H n.m.r. spectrum of this compound features an aromatic AA′BB′-multiplet characteristic of *ortho*-substituted phthalates,[17] accompanied by a deshielded four-proton doublet (δ 4.16, J 5.63 Hz). The latter is indicative of two equivalent methylene groups, each constituting part of two identical 17-proton aliphatic chains, positioned adjacent to methine protons. The magnetic non-equivalence of the terminal methyl groups (6 H each, triplets, δ 0.87, 0.91) broadened by long-range coupling, taken in conjunction with the above, rules out all possibilities but two 2-ethylhexyl ester groups. Mass spectral fragmentation yields the significant ions m/e 390 (1.8%; M^+), 279 (66; $M - C_8H_{16}$),* 167 (76; $M - 2 \times C_8H_{16}$),* 149 (100; $M - 2 \times C_8H_{16} - H_2O$), 113 (63; C_8H_{17}), 112 (34; C_8H_{16}), and 57 (C_4H_9), the last peak supporting the proposed branch chain structure (6).

Although bis-(2-ethylhexyl) phthalate may represent an artifact acquired during handling, the possibility of its natural existence finds support in the knowledge that several phthalic acid esters exist in *Oenanthe stofonifera*.[18] Commercial application of phthalate esters as insect repellents may well provide the key to their likely physiological function in nature.

EXPERIMENTAL

Unless otherwise stated n.m.r. spectra obtained by Fourier-transform and continuous-wave techniques were recorded for solutions in deuteriochloroform (Me_4Si as internal reference) and i.r. spectra for solutions in chloroform. Mass spectra were obtained with Varian CH-5 and MAT 311 A (field desorption) instruments. Hilger and Watts M 412 and JASCO J-20 spectropolarimeters were employed for optical rotation (in $CHCl_3$) and c.d. determinations (in MeOH) respectively.

Systems used for separation of components comprised Merck Kieselgel 60 (column chromatography) and Merck Kieselgel 60 PF 254 (preparative t.l.c.). T.l.c. bands were located by u.v. illumination and/or a spray reagent ($HClO_4$–$FeCl_3$).

Difficulties experienced with the retention of organic solvents by small quantities of non-crystalline compounds often led to unsatisfactory C and H analyses. In such cases reliance was placed on accurate mass determinations and purity assessed by n.m.r. spectroscopy.

Isolation of Constituents from P. angolensis.—Heartwood drillings (800 g) were successively extracted at ambient temperatures (*ca.* 25 °C) with n-hexane (3 × 3 l, 3 consecutive days) and methanol (3 × 3 l; 3 consecutive days), and an orange-red oil (11.3 g, 1.4%) and a dark brown resin (94.7 g, 11.8%), respectively, were obtained on evaporation of the solvents.

A portion of the n-hexane extract (6 g) was fractionated by column chromatography (length 75 cm × diam. 5 cm; benzene, flow rate 20 ml h^{-1}) into 11 crude fractions, the last two after limited addition of acetone to the eluant (benzene–acetone, 95 : 5). Two only of these, fraction 4 (retention time 48 h; 107 mg) and fraction 11 (retention time 111 h; 1.3 g) were further investigated. Initial purification of fraction 4 by t.l.c. (n-hexane–acetone, 9 : 1) produced a mixture of three compounds (R_F 0.54; 80 mg) which was resolved by subsequent t.l.c. separation (n-hexane–chloroform–methanol, 110 : 10 : 1; ×2) into (α*R*)-4-*O*-*T*-cadinylangolensin (4) (R_F 0.68), (α*R*)-4-*O*-α-cadinylangolensin (3) (R_F 0.59), and bis-(2-ethylhexyl) phthalate (6) (R_F 0.43). Fraction 11 yielded (α*R*)-angolensin (1) (retention time 25 h) after purification by column chromatography (85 cm × 1.5 cm; n-hexane–acetone 8 : 2; flow rate 20 ml h^{-1}).

Thirteen crude fractions were obtained from the fractionation of a portion of the methanol extract (12 g) by column chromatography (90 cm × 5 cm; benzene–acetone–methanol, 70 : 25 : 5; flow rate 20 ml h^{-1}). Fraction 3 (retention time 41 h, 6.77 g) from this fractionation required initial purification by column chromatography (75 cm × 5 cm; cyclohexane–acetone, 6 : 4; flow rate 20 ml h^{-1}), yielding crude (*S*)-4-*O*-methylangolensin (2) (retention time 33 h, 456 mg) from which the pure product was isolated by two successive t.l.c. separations (light petroleum–1,2-dichloroethane, 2 : 8; R_F 0.58 and cyclohexane–acetone, 9 : 1, × 4; R_F 0.57).

(αR)-4-O-α-*Cadinylangolensin* (3) crystallized from ethanol as white needles (35 mg), m.p. 136 °C (Found: C, 77.7; H, 8.5. $C_{31}H_{40}O_4$ requires C, 78.1; H, 8.5%); m/e 476 (M^+, field desorption), 341 (2.1%), 273 (28), 272 (47), 206 (21), 205 (91), 204 (90), 189 (10), 161 (63), 149 (39), 138 (22), 137 (100), 135 (91), 121 (90), 119 (17), 109 (18), 107 (21), 105 (35), 95 (25), 93 (25), 81 (70), 69 (30), 55 (22), 43 (12), and 41 (14); c.d. (c 0.052 0) $[\theta]_{224}$ 0, $[\theta]_{230}$ -3.8×10^4, $[\theta]_{239}$ 0, $[\theta]_{267}$ 3.9×10^4, $[\theta]_{279}$ 0, $[\theta]_{287}$ -1.7×10^4, $[\theta]_{322}$ -2.2×10^4, $[\theta]_{365}$ 0; ^1H and ^{13}C n.m.r. spectra, see Table 1 and refs. 19 and 20; $\nu_{max.}$ 1 635 cm^{-1} (C=O).

(αR)-4-O-T-*Cadinylangolensin* (4) was isolated as a colourless amorphous solid (15 mg), m.p. 44—46 °C; m/e 476 (M^+, field desorption), 341 (3.5%), 273 (23), 272 (56), 206 (22), 205 (86), 204 (53), 179 (12), 161 (33), 149 (41), 138 (26), 137 (100), 135 (86), 121 (86), 119 (14), 109 (23), 107 (24), 105 (33), 95 (31), 93 (25), 81 (84), 69 (36), 55 (29), 43 (18), and 41 (19); c.d. (c 0.048 0) $[\theta]_{225}$ 0, $[\theta]_{230}$ -3.7×10^4, $[\theta]_{240}$ 0, $[\theta]_{267}$ 3.8×10^4, $[\theta]_{281}$ 0, $[\theta]_{290}$ -0.82×10^4, $[\theta]_{235}$ -1.15×10^4, $[\theta]_{360}$ 0; ^1H and ^{13}C n.m.r. spectra see Table 1; $\nu_{max.}$ 1 635 cm^{-1} (C=O).

(αS)-4-O-*Methylangolensin* (2) crystallized from methanol as colourless needles (15 mg), m.p. 28—30 °C (Found: C, 71.2; H, 6.4. $C_{17}H_{18}O_4$ requires C, 71.3; H, 6.3%); m/e 286 (21%, M^+), 284 (37), 152 (36), 151 (100), 149 (61), 135 (54), 120 (5.8), and 105 (17); c.d. (c 0.052 8) $[\theta]_{225}$ 0, $[\theta]_{232}$ 3.5×10^4, $[\theta]_{241}$ 0, $[\theta]_{270}$ -1.9×10^4, $[\theta]_{283}$ 0, $[\theta]_{317}$ 1.15×10^4, $[\theta]_{365}$ 0; ^1H and ^{13}C n.m.r. spectra see Table 1; $\nu_{max.}$ 1 640 cm^{-1} (C=O).

(αR)-Angolensin (1) crystallized from benzene as colourless needles (570 mg), m.p. 122 °C (lit.,[10] 119 °C) (Found: M^+, 272.102. $C_{16}H_{16}O_4$ requires M, 272.105); m/e 272 (56%, M^+), 138 (48), 137 (100), 136 (36), 135 (79), 120 (13), and 105 (43); $[\alpha]_D^{26}$ $-119°$ (1.07% in MeOH) {lit.,[10] $[\alpha]_D^{32}$ $-120°$}; c.d. (c 0.052 1) $[\theta]_{225}$ 0, $[\theta]_{232}$ -4.2×10^4, $[\theta]_{241}$ 0, $[\theta]_{270}$ 3.6×10^4, $[\theta]_{281}$ 0, $[\theta]_{290}$ -1.4×10^4, $[\theta]_{300}$ -1.15×10^4, $[\theta]_{318}$ -1.6×10^4, $[\theta]_{365}$ 0; ^1H and ^{13}C n.m.r. spectra see Table 1 and refs. 19 and 20; $\nu_{max.}$ 1 640 cm^{-1} (C=O).

Bis-(2-ethylhexyl) phthalate (6) was obtained as a colourless oil (15 mg) (Found: m/e 279.158. $C_{16}H_{23}O_4$ requires m/e 279.159); m/e 390 (1.8%, M^+), 279 (67), 168 (22), 167 (76), 150 (62), 149 (100), 132 (7.9), 113 (63), 112 (33), 104 (17), and 83 (32); δ_H 7.53 (m, 4 H, ArH), 4.16 (d, J 5.63 Hz, 2 × OCH_2), 1.31 (m, 8 × CH_2 and 2 × CH), and 0.87 (m, 4 × CH_3); $\nu_{max.}$ 1 730 cm^{-1} (RO–C=O).

Crystallographic Analysis of (αR)-4-O-α-*Cadinylangolensin* (3).—Crystals of (α*R*)-4-*O*-α-cadinylangolensin (3), suitable for *X*-ray structure determination, were obtained by recrystallization from ethanol–water (125 : 10). Three-dimensional intensity data were collected on a modified Hilger-Watts 4-circle diffractometer, using graphite crystal-monochromated Cu-K_α radiation at room temperature. Peaks were scanned in the ω–2θ mode at a rate of 0.05 ω s^{-1} to cover 1.2 ω°, while the background was counted for 18 s at each end of the scans. The intensities were corrected for background and Lorentz polarization, and yielded 1 909 independent measurable reflections.

* Presumably accompanied by H-transfer.

TABLE 3

Final fractional co-ordinates ($\times 10^4$) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
C(1)	532(6)	5 313(19)	3 143(7)
C(2)	808(7)	5 113(23)	4 178(7)
C(3)	1 546(6)	3 373(25)	4 432(7)
C(4)	2 187(6)	3 749(23)	3 845(7)
C(5)	2 046(6)	5 070(23)	3 106(7)
C(6)	1 232(6)	6 326(21)	2 720(7)
C(7)	994(6)	6 368(20)	1 672(7)
C(8)	152(7)	7 645(24)	1 358(8)
C(9)	−562(6)	6 581(23)	1 778(7)
C(10)	−325(7)	6 462(21)	2 812(7)
C(11)	2 986(7)	2 404(27)	4 156(9)
C(12)	1 695(8)	7 205(25)	1 203(8)
C(13)	1 967(11)	9 766(29)	1 449(14)
C(14)	1 461(9)	6 886(35)	177(8)
C(15)	−344(7)	8 906(20)	3 290(8)
O(16)	−888(4)	4 856(14)	3 142(6)
C(17)	−1 704(6)	5 212(20)	3 175(7)
C(18)	−2 225(6)	7 068(21)	2 747(7)
C(19)	−3 065(7)	7 160(21)	2 845(7)
C(20)	−3 403(6)	5 522(18)	3 354(7)
C(21)	−2 870(7)	3 648(21)	3 746(7)
C(22)	−2 039(6)	3 552(20)	3 667(7)
O(23)	−3 136(5)	1 969(16)	4 240(5)
C(24)	−4 271(7)	5 551(23)	3 484(8)
O(25)	−4 558(5)	4 024(18)	3 898(6)
C(26)	−4 820(7)	7 658(23)	3 115(9)
C(27)	−5 477(9)	8 087(29)	3 730(10)
C(28)	−5 247(6)	7 225(23)	2 137(9)
C(29)	−5 204(8)	8 826(26)	1 480(11)
C(30)	−5 633(8)	8 543(28)	583(11)
C(31)	−6 108(7)	6 522(27)	310(9)
C(32)	−6 142(8)	4 884(24)	981(9)
C(33)	−5 725(7)	5 229(22)	1 874(9)
O(34)	−6 534(6)	6 146(22)	−548(7)
C(35)	−6 635(12)	7 974(34)	−1 199(11)
H(1)	427	3 555	2 892
H(2A)	1 010	6 800	4 456
H(2B)	284	4 520	4 462
H(3A)	1 301	1 624	4 331
H(3B)	1 847	3 611	5 141
H(5)	2 557	5 269	2 750
H(6)	1 323	8 138	2 903
H(7)	908	4 587	1 443
H(8A)	236	9 442	1 566
H(8A)	−29	7 550	621
H(9A)	−694	4 848	1 509
H(9B)	−1 119	7 645	1 586
H(11A)	2 901	1 398	4 740
H(11B)	3 499	3 616	4 365
H(11C)	3 132	1 253	3 639
H(12)	2 235	6 122	1 468
H(13A)	2 150	10 137	2 171
H(13B)	1 429	10 822	1 150
H(13C)	2 485	10 154	1 122
H(14A)	1 982	7 439	−121
H(14B)	925	8 001	−62
H(14C)	1 297	5 114	−23
H(15A)	160	9 965	3 139
H(15B)	−316	8 916	4 019
H(15C)	−944	9 598	2 940
H(18)	−1 978	8 377	2 356
H(19)	−3 466	8 542	2 513
H(22)	−1 641	2 161	3 996
H(23)	−3 667	2 296	4 350
H(26)	−4 436	9 198	3 133
H(27A)	−5 826	9 537	3 380
H(27B)	−5 260	8 515	4 443
H(27C)	−5 881	6 578	3 670
H(29)	−4 827	10 367	1 663
H(30)	−5 603	9 891	88
H(32)	6 503	3 311	801
H(33)	−5 769	3 921	2 380
H(35A)	−7 009	7 203	−1 810
H(35B)	−6 000	8 252	−1 294
H(35C)	−6 909	9 617	−1 068

The structure (Figure) was determined by direct methods and refined by full-matrix least squares, resulting in a final R value of 0.084. The SHELX-76 program [21] was used for all the crystallographic computations on a CDC CYBER 174.

The refined fractional co-ordinates are given in Table 3. All hydrogen atoms are numbered according to the atoms to which they are attached and a common isotropic temperature factor of 0.105 (0.013) Å^2 was refined for all. Bond lengths, bond angles, thermal parameters, torsion angles, deviations of non-hydrogen atoms from the best least-squares plane, and observed and calculated structure factors have been deposited in Supplementary Publication No. SUP 22816 (18 pp.).

Crystal data: $C_{31}H_{40}O_4$, monoclinic Pz_1, $a = 16.21(1)$, $b = 5.75(1)$, $c = 14.95(1)$ Å, $\beta = 101.9(5)°$, $U = 1\,364$ Å^3, $Z = 2$, μ(Cu-K_α) $= 5.18$ cm^{-1}.

The authors thank the South African C.S.I.R., Pretoria, and the Sentrale Navorsingsfonds of the University of the Orange Free State for financial support; Dr. U. Rapp, Varian MAT GmbH, Bremen, for field-desorption mass spectra; and Dr. W. E. Hull, Bruker Analytische Messtechnik GmbH, Rheinstetten am Silberstreifen, for 360-MHz ^{1}H n.m.r. spectra. One of us (B. C. B. B.) also acknowledges tenure of a C.S.I.R. research assistantship.

[9/1493 *Received, 20th September,* 1979]

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