Chemical Studies on the Annonaceae. Part 9.[1] Indolosesquiterpene and Aporphine Alkaloids from *Greenwayodendron* (*Polyalthia*) *suaveolens* Stem Bark. *X*-Ray Crystal Stucture of Greenwayodendrin-3-one

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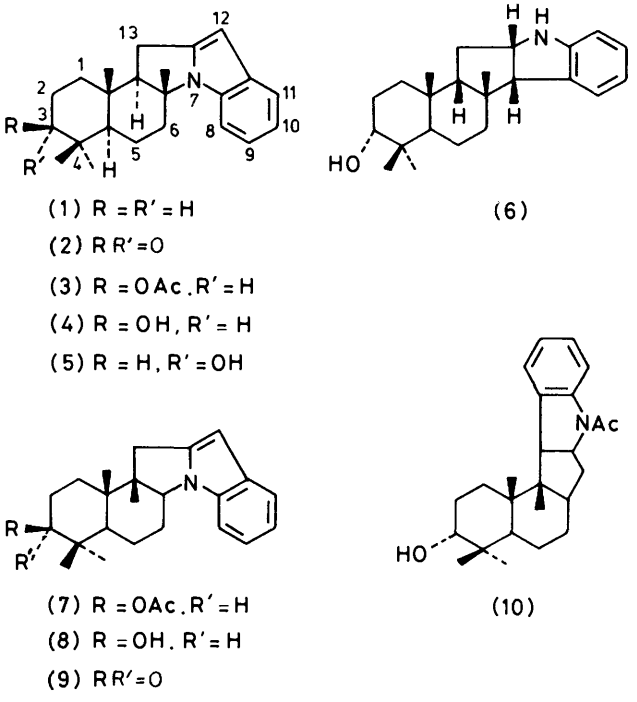
The isolation and characterization of ten alkaloids, *viz.* five indolosesquiterpenes and five aporphines, and the triterpene polycarpol from the stem bark of *G. suaveolens* are reported. Four of the indolosesquiterpenes are shown, largely on the basis of ^{1}H- and ^{13}C-n.m.r., to be based on the novel 1,3,4,4aα,5,6,6a,-13,13aα,13b-decahydro-4,4,6aβ,13bβ-tetramethyl-2*H*-benz[*e*]indolo[1,2-*a*]indole system (1) to which we have assigned the trivial name greenwayodendrine. The structure of one of the novel alkaloids is confirmed as greenwayodendrin-3-one (2) by *X*-ray crystallography, and by chemical interconversions the other three are identified as the 3α-hydroxy- (5), 3β-hydroxy- (4), and 3β-acetoxy- (3) derivatives.

Greenwayodendron suaveolens (Engl. & Diels) Verdc. (Annonaceae), previously known as *Polyalthia suaveolens* Engl. & Diels, is a West African rain-forest tree found from Nigeria to Angola.[2] An investigation of a sample of stem bark originating from the Republic of Congo Brazzaville [3,4] yielded ten 7-oxygenated aporphine alkaloids and the indolosesquiterpene polyveoline (6). More recently, Okorie [5] has reported the occurrence of four further indolosesquiterpenes, *viz.* polyavolensin (7), polyavolensinol (8), polyavolensinone (9), and polyavolinamide (10), from Nigerian material. Alkaloids (6)—(10) are, together with polyalthenol (11) from the closely allied *Greenwayodendron* (*Polyalthia*) *oliveri* (Engl.) Verdc.,[6] the only indolosesquiterpene alkaloids recorded to date.

We now report the results of an investigation of the stem bark of *G. suaveolens* collected in the Korup Forest Reserve in West Cameroon. Of the ten alkaloids isolated, four, namely polyveoline (6) and the aporphines polysuavine (12), oliverine (13), and oxostephanine (14) which last three were isolated by acid/base partition of concentrated chloroform and methanol extracts followed by preparative layer chromatography (p.l.c.) of the mixed bases, were already known from this species.[3] Two others, the *N*-oxides of oliverine (13) and oliveridine (15) [*i.e.* compounds (16) and (17)], gave spectral data in complete agreement with those previously reported for the *N*-oxides isolated from the allied species *Enantia pilosa* Exell.[7] The four remaining alkaloids were shown to possess a novel pentacyclic ring system, which we have termed the greenwayodendrine nucleus (1), and were characterised as compounds (2)—(5) on the basis of their chemical interconversion and a detailed analysis of their spectral data, notably the 360 MHz ^{1}H n.m.r. data. The structure of compound (2), although not its absolute configuration, was subsequently confirmed by *X*-ray crystallography. In addition to the alkaloids, the presence of the triterpene polycarpol (18), previously reported from *G. oliveri*,[8] was also identified.

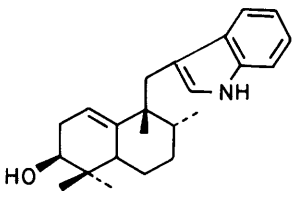
The initial light-petroleum † extract of the bark yielded seven compounds. P.l.c. of the basic fraction gave compounds (6) and (13). Similar treatment of the neutral fraction gave compound (18) and the four novel indolosesquiterpenes (2)—(5). The relationship between compounds (2)—(5) was established as follows. Acetylation of the alcohol (4) gave its acetate (3) and reduction of the ketone (2) with sodium borohydride gave a mixture of the alcohols (4) and (5) in a *ca.* 9 : 1 ratio. On this basis compound (3) must be the acetate of compound (4), and compound (2) the derived ketone of compounds (4) and (5). Compounds (4) and (5) must be the two possible hydroxy-epimers derived from compound (2).

Compound (4) exhibited u.v. and i.r. spectral characteristics indicative of an indole nucleus and an alcoholic hydroxy-group, respectively. Accurate mass measurement suggested it had the molecular formula $C_{23}H_{31}NO$ and, under electron-impact fragmentation, it gave a base peak of *m/z* 130 ($C_9H_8N^+$)

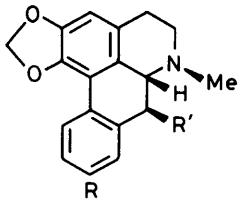


Systematic benz[*e*]indolo[1,2-*a*]indole numbering scheme for the greenwayodendrines (1)—(5) [and the polyavolensines (7)—(9)]

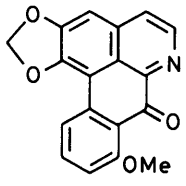
† Light petroleum refers to that fraction boiling in the range 40—60 °C.



(11)



(12) R = OH, R' = OMe
(13) R = R' = OMe
(15) R = OMe, R' = OH



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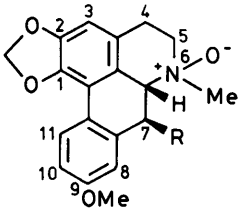
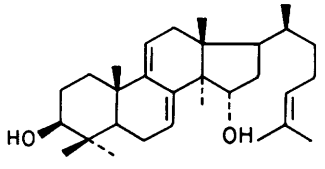
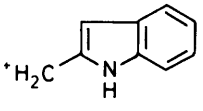


(16) R = OH
(17) R = OMe

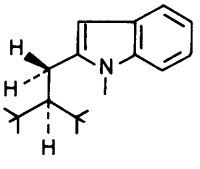


(18)

Systematic dibenzo[*de*,*g*]quinoline numbering scheme for the aporphines (12)—(17)



(19)



(20)

due to ion (19). Both the ^{1}H- and ^{13}C-n.m.r. spectra clearly indicated the presence of an indole nucleus substituted at N-1 and C-2.

By subtraction of C_8H_5N the non-indolic portion of compound (4) must be $C_{15}H_{26}O$ which, in the absence of further centres of unsaturation, must take the form of a tricyclic unit and, in view of previous reports of indolosesquiterpene alkaloids from this species, is probably of sesquiterpene origin. The ^{1}H n.m.r. spectrum (Table 1) showed signals for four tertiary methyl groups and an oxymethine proton at δ 3.25. A series of decoupling experiments revealed an ABX system centred at δ 2.22 (X), 2.68, and 2.82, the X-proton showing axial–axial coupling (*J* 12.5 Hz). The ABX system showed no further coupling, requiring it to be due to an isolated $-C\cdot CH_2\cdot CH_{ax}\cdot C-$ unit. The chemical shifts for the methylene protons of the ABX system exhibited marked deshielding, indicating proximity to the indole nucleus. The absence of a strongly deshielded secondary carbon atom signal in the ^{13}C n.m.r. spectrum precluded the presence of an NCH_2 moiety, thus requiring attachment of the CH_2 to C-2 of the indole, as in structure (6), and allowing the assignment of the partial structure (20).

The hypothesis that compound (4) was similar to compound (6), but with N-1 (rather than C-3) of the indole forming the second link to the sesquiterpene, was sustained by the ^{13}C n.m.r. spectrum of compound (4). In addition to the signal for the hydroxy-bearing carbon atom, two deshielded resonances were observed for the non-indolic portion of compound (4), *viz.* a tertiary carbon at δ_C 65.2 and a quaternary carbon at δ_C 63.0 p.p.m. The former can be assigned to C-13a which is typically deshielded in decalins with the same substitution pattern as in compounds (2)—(5),[9] and which must be tertiary (X of ABX). The latter will be due to C-6a, deshielded by being bonded to N-7 (N-1 of indole), and which must, because of its quaternary nature, carry one of the methyl substituents. The methyl resonance at δ 1.22 in the ^{1}H n.m.r. spectrum can be assigned to the 6a-*Me*, the three remaining methyl signals being typical of C-4 *gem*-dimethyl and C-13b methyl groups found in the sesquiterpene moieties of other indolosesquiterpenes.[4–6]

The OH substituent of compound (4) was assigned to C-3 and to an equatorial configuration on the basis of the following data. The oxymethine proton of compound (4) was observed as a double doublet at δ_H 3.25 showing axial–axial coupling (*J* 10 Hz). This consigned the OH to the equatorial configuration and restricted its placement to those positions (C-1, -3, or -6) where the oxymethine proton could only interact with two other protons. The pronounced changes observed in the resonance positions of the C-4 methyls and, to a lesser extent, the C-13b methyl on conversion of compound (4) into compounds (2) and (3) (Table 1) can only be accounted for by assuming the presence of a ' biogenetically normal ' 3-OH substituent.[5,6,10] The ^{13}C n.m.r. spectra of both compounds (2) and (4) gave signals in close agreement with published data for the A-rings of the corresponding decalone and decalol, respectively.[11]

The remaining problems concern the stereochemistry of compounds (2)—(5) at C-4a, -6a, and -13b. The following observations indicate that the A/B ring junction (C-4a)/(C-13b) is *trans*-fused and that both the 6a- and 13b-methyl groups are axial, as in structure (6).[4] (i) The 4a-H atom is observed as a double doublet at δ 1.27 and 1.63 in compounds (4) and (2), respectively (Table 1). In both cases the large coupling constant (*J* 12 Hz) suggests axial–axial interaction involving this proton. (ii) The resonance position of the 13b-methyl hydrogen in compound (4) (δ 1.06) is typical of that of the 10-methyl of kaurane diterpenes in which that group undergoes 1,3-diaxial interaction with the C-12 (methylene) group [equivalent to C-12a in structure (4)]. By contrast the 10-methyl signal occurs at δ *ca.* 0.89 in the absence of this interaction.[12] In structure (4) this interaction cannot be with the equivalent of the kaurane C-12 (methylene) group but must be with an axial methyl at C-6a, thus requiring both methyls to be axial. (iii) In the ^{1}H n.m.r. spectra of both compounds (2) and (4) a triplet of doublets at δ 2.72—2.74 can be assigned to 6-H_{eq}. The strong deshielding of this proton relative to 6-H_{ax} (δ *ca.* 2.05) must be caused by it lying in the plane of the indole aromatic nucleus; this would occur when the 6a-methyl is axial. By contrast, 6-H_{ax} is directed out of that plane. On the other hand, if the 6a-methyl were to be placed in the equatorial position then both 6-protons would lie near the plane of the aromatic ring and would be expected to suffer a similar degree of deshielding. (iv) Finally, if the 6a-methyl were equatorial and the terpene retained the normal chair form, the dihedral angle between the 13- and 13a-H would be about 45° in each case and could not explain the observed *J* value of 12.5 Hz.

Table 1. ^{1}H N.m.r. spectra of compounds (2), (3), and (4)

	(2) [a]	(3) [b]	(4) [a]
13a-H_{ax}	2.26 (dd, *J* 12.7 and 6.4 Hz)	2.22 (dd, *J* 12.0 and 7.0 Hz)	2.22 (dd, *J* 12.5 and 6.5 Hz)
13-H_{ax}	2.72 (dd, *J* 14.9 and 12.7 Hz)	2.74 (m)	2.68 (dd, *J* 15.0 and 12.5 Hz)
13-H_{eq}	2.85 (dd, *J* 14.9 and 6.4 Hz)	2.74 (m)	2.82 (dd, *J* 15.0 and 6.5 Hz)
9-, 10-, and 11-H	7.02, 7.09, 7.32 (m, 3 H)	7.00—7.40 (m, 3 H)	7.02, 7.09, 7.34 (m, 3 H)
8-H	7.55 (dd, *J* 9 and 3 Hz)	7.60 (dd, *J* 9 and 3 Hz)	7.55 (dd, *J* 9 and 3 Hz)
6-H_{ax}	2.05 (dt, *J* 12.2 and 3.5 Hz)		2.04 (dt, *J* 12.0 and 3.9 Hz)
6-H_{eq}	2.74 (td, *J* 12.0 and 3.5 Hz)	2.74 (m)	2.72 (td, *J* 12.0 and 3.2 Hz)
5-H_{ax}	1.77 (dq, *J* 12.8 and 3.5 Hz)		1.63 (m)
5-H_{eq}	1.89 (qd, *J* 13.0 and 3.5 Hz)		1.97 (qd, *J* 12.0 and 3.6 Hz)
4a-H_{ax}	1.63 (dd, *J* 12.0 and 3.5 Hz)		1.27 (dd, *J* 12.0 and 5.0 Hz)
3-H_{ax}		4.54 (dd, *J* 10.0 and 6.0 Hz)	3.25 (dd, *J* 10.0 and 5.4 Hz)
2-H_{ax}	2.63 (ddd, *J* 16.6, 10.2, and 3.5 Hz)		1.52—1.75 (m, 4 H)
2-H_{eq}	2.52 (ddd, *J* 16.6, 7.5, and 3.5 Hz)		
1-H_{ax}	1.65 (ddd, *J* 15.0, 10.2, and 3.5 Hz)		
1-H_{eq}	1.87 (ddd, *J* 15.0, 7.5, and 3.5 Hz)		
13b-Me_{ax}	1.17 (s)	1.10 (s)	1.06 [c] (s)
6a-Me_{ax}	1.24 (s)	1.21 (s)	1.22 (s)
4-Me_2	1.13, 1.15 (2 × s)	0.95 (s, 6 H)	0.88, 1.05 [c] (2 × s)
3-OAc		2.07 (s)	

All spectra were run in $CDCl_3$. [a] 360 MHz. [b] 90 MHz. [c] Signals interchangeable.

On the basis of the above data the novel alkaloids (2)—(4) were assigned the nucleus (1) to which we have given the trivial name of greenwayodendrine; compounds (2), (3), and (4) were then identified as greenwayodendrin-3-one, greenwayodendrin-3β-yl acetate, and greenwayodendrin-3β-ol, respectively. A fourth novel alkaloid was isolated in trace amounts only. Its identification as greenwayodendrin-3α-ol (5) rests entirely on its t.l.c. co-identity with the minor reduction product obtained from compound (2) by treatment with sodium borohydride. It is interesting to note that the stereochemistry of compounds (2)—(4) differs from that of compound (6) at C-13a.

The structure of compound (2) was finally confirmed by *X*-ray crystallography. The molecule is depicted in the Figure, which also shows the crystallographic numbering scheme. The blade-like monoclinic crystals were thinnest in the *b* direction. A specimen of dimensions 0.67 × 0.67 × 0.07 mm was selected for data collection on an Enraf-Nonius CAD4 diffractometer with monochromated Mo-K_α radiation, λ 0.710 69 Å.

Crystal Data.—Compound (2), $C_{23}H_{29}NO$, M = 335.22. Monoclinic, a = 7.426(2), b = 9.319(1), c = 13.975(4) Å, β = 104.19(2)°, U = 937.6(4) Å^3, Z = 2, D_c = 1.19 g cm^{-3}, $F(000)$ = 362, μ(Mo-K_α) = 0.38 mm^{-1}. Space group $P2_1$.

Structural Analysis.—Intensity data were collected by the ω–2θ scan technique with the crystal oriented for minimum absorption (Enraf-Nonius option FLAT). Of the 1 748 unique reflections measured, 1 426 were deemed observed ($F > 3\sigma$). After all non-hydrogen atoms had been located in an *E*-map phased by MULTAN [13] and then refined, the hydrogen atoms were entered in calculated positions with the isotropic temperature factors of their attached atoms. Refinement of co-ordinates and anisotropic thermal parameters for non-hydrogen atoms, with methyl groups treated as rigid bodies free to rotate, was carried out with SHELX,[14] reducing the discrepancy index to R 0.047 for the observed data. Reflections were weighted by $w = k/[\sigma^2(F_o) + gF_o^2]$, where g is a variable parameter adjusted after each cycle; it converged to 8 × 10^{-6}. A difference electron-density map displayed no feature greater than 0.16 e Å^{-3}. Observed and calculated structure factors, hydrogen co-ordinates, and atomic thermal parameters are given in Supplementary Publication No. SUP 23410 (12 pp.).*

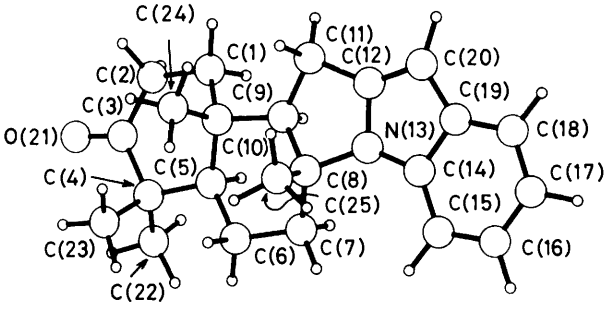


Figure. View of greenwayodendrin-3-one (2), projected onto the least-squares plane of the molecule, showing the crystallographic numbering scheme

Atomic co-ordinates are given in Table 2. The ring skeleton forms a ridged surface almost perpendicular to the *b* axis with *y*-co-ordinates ranging over only $\frac{1}{8}$th of the unit-cell length. It is fully extended along the *a*–*c* diagonal, covering $\frac{3}{4}$ of the unit cell. Such extended geometry is possible because the ring fusion at the A/B junction is *trans*, leaving the methyl groups C(24)H_3 and C(25)H_3 † to occupy axial positions. Their close proximity [3.213(6) Å] makes interaction feasible and

* For details of Supplementary Publications see Notice to Authors No. 7, *J. Chem. Soc., Perkin Trans. I*, 1981, Index issue.
† Crystallographic numbering scheme.

Table 2. Final atomic co-ordinates (× 10^4) for C, N, and O atoms of compound (2), with standard deviations in parentheses

Atom [a]	x/a	y/b	z/c
C(1)	1 992(5)	−1 752(8)	2 876(3)
C(2)	2 179(7)	−1 566(11)	3 981(3)
C(3)	563(6)	−1 541(7)	4 370(3)
C(4)	−1 416(6)	−1 521(6)	3 719(3)
C(5)	−1 396(5)	−1 501(6)	2 605(2)
C(6)	−3 357(5)	−1 734(7)	1 916(2)
C(7)	−3 391(5)	−1 548(6)	817(2)
C(8)	−2 026(5)	−2 584(6)	551(2)
C(9)	−105(4)	−2 257(6)	1 222(2)
C(10)	120(5)	−2 454(6)	2 342(2)
C(11)	1 285(5)	−2 926(6)	689(2)
C(12)	251(5)	−2 702(6)	−376(2)
N(13)	−1 558(4)	−2 305(0)	−398(2)
C(14)	−2 552(5)	−2 244(6)	−1 369(2)
C(15)	−4 416(6)	−1 914(6)	−1 774(3)
C(16)	−5 018(7)	−1 869(7)	−2 794(3)
C(17)	−3 796(7)	−2 124(7)	−3 381(3)
C(18)	−1 948(7)	−2 435(6)	−2 987(3)
C(19)	−1 294(5)	−2 514(5)	−1 959(3)
C(20)	475(6)	−2 806(6)	−1 299(3)
O(21)	819(5)	−1 555(8)	5 246(2)
C(22)	−2 290(9)	−126(8)	3 978(4)
C(23)	−2 493(7)	−2 801(8)	4 022(3)
C(24)	110(8)	−4 014(6)	2 649(3)
C(25)	−2 712(7)	−4 130(6)	502(3)

[a] Crystallographic numbering scheme.

C(2) atom is also enlarged, to 120.6(4)°. At C(5) all three C–C–C angles exceed the tetrahedral value, thus squeezing the 5-H atom. Distortion of ring C occurs by angle deformation as indicated by the N(13)–C(8)–C(9) angle of only 97.2(3)° and the C(12)–C(11)–C(9) angle of 100.4(3)°. As expected, bond distances in the indole system are consistent with extensive delocalization.

Finally it is necessary to draw attention to the close similarity between data reported here for the greenwayodendrines (2)—(4) and those published [5] for the polyavolensine series (7)—(9). The structures assigned for the latter alkaloids, based mainly on ^{1}H- and ^{13}C-n.m.r. data, differ from those assigned to compounds (2)—(4) in placing a methyl substituent at C-13a and not at C-6a. An expected feature of the ^{1}H n.m.r. spectra of compounds (7)—(9) would be a deshielded AB quartet for 13-H_2 [*cf.* compound (11)[6]] but no mention of this is made.[5] Furthermore the ^{13}C n.m.r. spectra of compounds (7) and (8) show [5] deshielded tertiary and quaternary carbons very similar to those seen for compounds (2) and (4). Whilst the tertiary resonance at δ_C *ca.* 65.0 p.p.m. for compounds (7) and (8) could be assigned to C-6a, the quaternary resonance at δ_C *ca.* 63.0 p.p.m. is *ca.* 20 p.p.m. deshielded compared with that expected for C-13a in analogous systems [*cf.* compound (11)[6] and clerodane diterpenes [15]]. In both the light of the above facts and the absence of other confirmatory data it seems prudent to regard the occurrence of compounds (7)—(9) in *G. suaveolens* as doubtful at present. Unfortunately, our attempts to obtain samples of the alkaloids (7)—(9) for direct comparison were unsuccessful.

Table 3. Selected torsion angles (°) for atoms of compound (2). Crystallographic numbering scheme used

C(4)–C(5)–C(10)–C(9)	−179.4	C(8)–C(9)–C(10)–C(24)	71.3
C(6)–C(5)–C(10)–C(1)	163.1	C(6)–C(7)–C(8)–C(25)	72.6
C(6)–C(5)–C(10)–C(9)	49.7	C(25)–C(8)–C(9)–C(10)	−65.8
C(10)–C(5)–C(6)–C(7)	−54.4	C(7)–C(8)–C(9)–C(11)	−160.2
C(5)–C(6)–C(7)–C(8)	57.5	N(13)–C(8)–C(9)–C(10)	−178.2
C(6)–C(7)–C(8)–C(9)	−58.5	C(11)–C(12)–N(13)–C(14)	−173.9
C(7)–C(8)–C(9)–C(10)	62.2	C(20)–C(12)–N(13)–C(8)	163.3
C(8)–C(9)–C(10)–C(5)	−55.8	N(13)–C(14)–C(19)–C(18)	−176.6
C(6)–C(5)–C(10)–C(24)	−76.1	C(15)–C(14)–C(19)–C(20)	179.8

Table 4. Interatomic distances (Å) for C, N, and O atoms of compound (2), with standard deviations in parentheses. Crystallographic numbering scheme used

C(1)–C(2)	1.526(6)	C(9)–C(10)	1.544(4)
C(1)–C(10)	1.552(6)	C(9)–C(11)	1.545(5)
C(2)–C(3)	1.434(6)	C(10)–C(24)	1.516(6)
C(3)–O(21)	1.192(4)	C(11)–C(12)	1.513(5)
C(3)–C(4)	1.527(5)	C(12)–N(13)	1.386(4)
C(4)–C(22)	1.535(7)	C(12)–C(20)	1.344(5)
C(4)–C(23)	1.552(7)	N(13)–C(14)	1.378(4)
C(4)–C(5)	1.561(5)	C(14)–C(15)	1.395(5)
C(5)–C(6)	1.552(5)	C(14)–C(19)	1.412(5)
C(5)–C(10)	1.547(5)	C(15)–C(16)	1.386(5)
C(6)–C(7)	1.540(5)	C(16)–C(17)	1.385(7)
C(7)–C(8)	1.511(5)	C(17)–C(18)	1.378(6)
C(8)–C(9)	1.533(5)	C(18)–C(19)	1.401(5)
C(8)–N(13)	1.474(4)	C(19)–C(20)	1.434(5)
C(8)–C(25)	1.524(6)		

this may be seen in the ^{1}H n.m.r. spectrum. Torsion angles (Table 3) prove the chair conformation for the B-ring inferred from spectroscopic results. Bond distances (Table 4) and angles (Table 5) are consistent with the observed spectral features. The presence of a carbonyl group is confirmed, with a C=O bond distance of 1.192(4) Å; its intra-annular bond angle exceeds 120°. The adjacent angle at the tetrahedral

Experimental

The stem bark of *Greenwayodendron suaveolens* was collected in the Korup Forest Reserve, Cameroon, in the summer of 1979. A voucher specimen, D. W. Thomas 725, has been deposited at the Herbarium of the Royal Botanic Gardens, Kew. U.v. spectra were recorded with a Unicam SP 800A spectrophotometer, and i.r. spectra with a Perkin-Elmer 157 spectrophotometer. ^{1}H N.m.r. spectra were recorded with either a Perkin-Elmer R32B (90 MHz) or a Brucker WH-360 (360 MHz) spectrometer, and ^{13}C spectra on either a JEOL PFT-100 (25.1 MHz) or Brucker WH-360 (90.56 MHz) spectrometer. Tetramethylsilane was used as internal standard for all n.m.r. spectra. Mass spectra were recorded on an A.E.I. MS902 double-focusing instrument. Silica gel G (Merck) was used for t.l.c. and silica gel (Merck, 30—70 mesh) was used for column chromatography. M.p.s were determined with a Kofler hot-stage apparatus.

Extraction of the Stem Bark of G. suaveolens.—The powdered stem bark (120 g) was extracted successively with light petroleum, chloroform, and methanol. The light-petroleum extract was washed with 2M HCl to separate basic and non-basic fractions. The HCl-soluble fraction was basified with NH_4OH and extracted into diethyl ether. P.l.c. of the ethereal extract gave, on development with chloroform–

Table 5. Interatomic angles (°) for C, N, and O atoms of compound (2), with standard deviations in parentheses. Crystallographic numbering scheme used

C(10)–C(1)–C(2)	112.5(4)	C(5)–C(10)–C(1)	105.2(3)
C(3)–C(2)–C(1)	120.6(4)	C(9)–C(10)–C(1)	107.4(3)
C(4)–C(3)–C(2)	123.2(3)	C(9)–C(10)–C(5)	105.6(3)
O(21)–C(3)–C(2)	116.8(4)	C(24)–C(10)–C(1)	109.5(4)
O(21)–C(3)–C(4)	120.0(4)	C(24)–C(10)–C(5)	115.4(4)
C(5)–C(4)–C(3)	110.6(3)	C(24)–C(10)–C(9)	113.2(3)
C(22)–C(4)–C(3)	105.7(4)	C(12)–C(11)–C(9)	100.4(3)
C(23)–C(4)–C(3)	108.2(4)	N(13)–C(12)–C(11)	108.3(3)
C(22)–C(4)–C(5)	109.5(4)	C(20)–C(12)–C(11)	141.4(3)
C(23)–C(4)–C(5)	114.4(3)	C(20)–C(12)–N(13)	110.2(3)
C(23)–C(4)–C(22)	108.1(4)	C(12)–N(13)–C(8)	112.0(3)
C(6)–C(5)–C(4)	112.4(3)	C(14)–N(13)–C(8)	134.9(3)
C(10)–C(5)–C(4)	114.6(3)	C(14)–N(13)–C(12)	108.4(3)
C(10)–C(5)–C(6)	113.5(3)	C(15)–C(14)–N(13)	130.3(4)
C(7)–C(6)–C(5)	112.7(3)	C(19)–C(14)–N(13)	107.2(3)
C(8)–C(7)–C(6)	109.0(3)	C(19)–C(14)–C(15)	122.3(3)
C(9)–C(8)–C(7)	107.6(3)	C(16)–C(15)–C(14)	117.5(4)
N(13)–C(8)–C(7)	115.4(3)	C(17)–C(16)–C(15)	120.7(4)
N(13)–C(8)–C(9)	97.2(3)	C(18)–C(17)–C(16)	122.2(4)
C(25)–C(8)–C(7)	112.2(4)	C(19)–C(18)–C(17)	118.8(4)
C(25)–C(8)–C(9)	117.8(3)	C(18)–C(19)–C(14)	118.5(4)
C(25)–C(8)–N(13)	106.0(3)	C(20)–C(19)–C(14)	106.9(3)
C(10)–C(9)–C(8)	116.7(3)	C(20)–C(19)–C(18)	134.6(4)
C(11)–C(9)–C(8)	104.9(3)	C(19)–C(20)–C(12)	107.1(3)
C(11)–C(9)–C(10)	121.5(3)		

methanol (19 : 1 v/v), compounds (6) (40 mg) and (13) (40 mg), both previously isolated from this species.[3,4] Column chromatography of the neutral fraction gave, on gradient elution with light petroleum containing increasing amounts of ethyl acetate, the acetate (3), the ketone (2), a mixture (A), the alcohol (4), polycarpol (18), and a second mixture (B). P.l.c. of mixture (A) gave compounds (2) and (5) and β-sitosterol. Similar treatment of mixture (B) gave a second crop of polycarpol (18).

A similarly prepared basic fraction of the chloroform concentrate was separated by p.l.c. [methanol–chloroform (3 : 1) as developer] to give the ketone (14) (12 mg), previously isolated from this species,[3] the *N*-oxide (16), and a trace of compound (17).

Identical treatment of the methanol concentrate yielded the aporphines (13) (110 mg) and (12) (10 mg), both previously reported from this species,[3] and a further crop of the *N*-oxide (17).

Identification of Greenwayodendrin-3β-yl Acetate (3).—This compound was recrystallised from light petroleum–ethyl acetate to give plates (20 mg), m.p. 211—214 °C; $[\alpha]_D^{25}$ −1.2° (*c*, 0.5 in $CHCl_3$); $\lambda_{max.}$ (EtOH) 227, 277, 282, and 292 nm; $\nu_{max.}$ (KCl) 1 730 and 1 610 cm^{-1}; ^1H n.m.r. data—see Table 1 (Found: M^+, 379.2517. $C_{25}H_{33}NO$ requires *M*, 379.2511); *m/z* 379 (68%), 364 (2), 131 (16), and 130 (100).

Identification of Greenwayodendrin-3-one (2).—This compound was recrystallised from light petroleum–ethyl acetate to give needles (110 mg), m.p. 191—194 °C; $[\alpha]_D^{25}$ +46.8° (*c*, 0.64 in $CHCl_3$) (Found: C, 82.4; H, 9.0; N, 4.2. $C_{23}H_{29}NO$ requires C, 82.4; H, 8.7; N, 4.2%); $\lambda_{max.}$ ($\log_{10}$ ε) (EtOH) 225 (4.63), 276 (3.88), 282 (3.89), and 293 nm (3.76); $\nu_{max.}$ (KCl) 1 700 and 1 610 cm^{-1}; ^1H n.m.r. data—see Table 1; δ_C ($CDCl_3$; 25.1 MHz) 15.5 (q, 13b-*Me*), 19.7 (q, 6a-*Me*), 20.8 (q, 4-Me_{ax}), 21.2 and 22.8 (2 × t, C-5 and -13), 26.9 (q, 4-Me_{eq}), 33.8 (t, C-2), 36.2 (s, C-13b), 37.8 and 38.2 (2 × t, C-6 and -1), 47.4 (s, C-4), 55.0 (d, C-4a), 63.0 (s, C-6a), 64.4 (d, C-13a), 94.8 (d, C-12), 109.6 (d, C-8), 119.4 (d, C-11), 120.7 and 121.0 (2 × d, C-9 and C-10), 132.1 (s, C-11a), 133.0 (s, C-7a), 142.8 (s, C-12a), and 216.7 p.p.m. (s, C-3) (Found: M^+, 335.2198. $C_{23}H_{29}NO$ requires *M*, 335.2249); *m/z* 335 (100%), 320 (52), 182 (17), 170 (12), 168 (17), 167 (13), 144 (10), 131 (25), 130 (92), and 117 (14).

Reduction of Greenwayodendrin-3-one (2).—A solution of the ketone (2) (9 mg) in EtOH (5 ml) was treated with $NaBH_4$ (5 mg) at room temperature for 2 h. The mixture was then acidified with 2M HCl (5 ml) and after normal work-up gave a mixture of the α- and β-hydroxy-epimers (5) and (4) in a *ca.* 1 : 9 ratio [R_F (α-epimer) 0.42; (β-epimer) 0.34; toluene–ethyl acetate–acetic acid (40 : 9 : 1) as developer]. The i.r. and ^1H n.m.r. spectra of the mixture were essentially those of the β-epimer (see below).

Identification of Greenwayodendrin-3β-ol (4).—This compound was recrystallised from light petroleum–chloroform to give long needles (20 mg), m.p. 167—169 °C; $[\alpha]_D^{27}$ +11° (*c*, 0.56 in $CHCl_3$); $\lambda_{max.}$ (EtOH) 227, 277, 282, and 293 nm; $\nu_{max.}$ (KCl) 3 425 and 1 610 cm^{-1}; ^1H n.m.r. data—see Table 1; δ_C ($CDCl_3$; 90.56 MHz) 15.0 (q, 13b-*Me*), 16.0 (q, 6a-*Me*), 19.8 (t, C-5), 20.0 (q, 4-Me_{ax}), 22.6 (t, C-13), 27.0 (t, C-2), 28.0 (q, 4-Me_{eq}), 36.4 (s, C-4), 37.9 and 38.4 (2 × t, C-6 and -1), 38.8 (s, C-13b), 55.9 (d, C-4a), 63.0 (s, C-6a), 65.2 (d, C-13a), 78.8 (d, C-3), 94.3 (d, C-12), 109.5 (d, C-8), 118.8 (d, C-11), 120.1 and 120.5 (2 × d, C-10 and -9), 131.8 (s, C-11a), 132.6 (s, C-7a), and 142.8 p.p.m. (s, C-12a) (Found: M^+, 337.2406. $C_{23}H_{31}NO$ requires *M*, 337.2355); *m/z* 337 (67%), 322 (21), 189 (8), 182 (25), 170 (19), 168 (22), 167 (14), 163 (19), 144 (19), 135 (16), 131 (53), 130 (100), and 117 (23).

Acetylation of Greenwayodendrin-3β-ol (4).—A solution of the alcohol (6 mg) in dry pyridine (0.4 ml) was treated with acetic anhydride at 40 °C for 16 h. The usual work-up gave a product (5 mg, 38 %), m.p. 211—214 °C, identical (u.v., i.r., ^1H n.m.r., t.l.c.) in all respects with the ester (3).

Identification of Greenwayodendrin-3α-ol (5).—This compound was obtained as a gum (2 mg) and could not be crystallised (Found: M^+, 337.2417. $C_{23}H_{31}NO$ requires *M*,

337.2406); *m/z* 337 (45%), 324 (10), 182 (25), 170 (5), 144 (5), 131 (5), 130 (100), and 117 (5). The u.v. spectrum was identical with that of the epimer (4). The t.l.c. characteristics of the alcohol (5) were identical (3 separate developing systems) with those of the minor product produced by the reduction of the ketone (2).

Identification of Polycarpol (18).—This compound was recrystallised from methanol as needles (125 mg), m.p. 171—174 °C (lit.,[8] 173—174 °C); $[\alpha]_D^{25}$ +100° (lit.,[8] +90°); $\lambda_{max.}$ (EtOH) 236, 243, and 252 nm; $\nu_{max.}$ (KCl) 3 450 cm^{-1}; δ ($CDCl_3$; 90 MHz) 0.62 (3 H, s, 18-H_3), 0.89 (3 H, s, 19-H_3), 0.91 (3 H, d, *J* 7 Hz, 21-H_3), 0.95 (3 H, s, 30-H_3), 1.01 (total 6 H, s, 28- and 29-H_3), 1.61 and 1.69 (2 × 3 H, 2 × s, 26- and 27-H_3), 3.27 (1 H, dd, *J* 11 and 6 Hz, 3-H), 4.30 (1 H, m, 15-H), 5.10 (1 H, t, *J* 7 Hz, 24-H), 5.30 (1 H, m, 11-H), and 5.87 (1 H, m, 7-H) (Found: M^+, 440.3649. $C_{30}H_{48}O_2$ requires *M*, 440.3654); *m/z* 440 (100%), 422 (1), 407 (7), 327 (2), 311 (1), 273 (2), 133 (2), 132 (2), and 119 (4).

Identification of Oliverine N-*Oxide* (17).—This compound was recrystallised from ethanol as brown-yellow needles (7 mg), m.p. 110—114 °C (lit.,[7] 134 °C from 1,2-dichloroethane); $[\alpha]_D^{25}$ +90° (lit.,[7] +110°); $\lambda_{max.}$ (EtOH) 223, 240, 283, and 315 nm; δ ($CDCl_3$; 90 MHz) * 2.82 (3 H, s, NMe), 3.57 (3 H, s, 7-OMe), 3.87 (3 H, s, 9-OMe), 4.50 and 5.15 (total 2 H, ABq, *J* 6 Hz, 6a- and 7-H), 6.07br (2 H, s, OCH_2O), 6.63 (1 H, s, 3-H), 6.95 (1 H, dd, *J* 9 and 3 Hz, 10-H), 7.10 (1 H, d, *J* 3 Hz, 8-H), and 8.17 (1 H, d, *J* 9 Hz, 11-H) (Found: M^+, 355.1435. $C_{20}H_{21}NO_5$ requires 355.1420); *m/z* 355 (6%), 339 (41), 337 (7), 325 (43), 324 (88), 322 (21), 310 (24), 296 (100), 295 (82), 281 (21), 265 (16), and 253 (7). In view of the marked difference in m.p. between that of the isolated material and that published for compound (17) a synthetic sample of compound (17) was prepared by the *N*-oxidation of oliverine (13) with H_2O_2 using the method of Nieto *et al.*[7] The product obtained was identical in all respects with the material isolated.

Identification of Oliveridine N-*Oxide* (16).—This compound was obtained as a brown gum (10 mg) and could not be crystallised; $\lambda_{max.}$ (EtOH) 225, 275, and 320sh nm; δ ($CDCl_3$; 90 MHz) 3.30 (3 H, s, NMe), 3.87 (3 H, s, 9-OMe), 6.80 (1 H, dd, *J* 9 and 3 Hz, 10-H), 7.10 (1 H, d, *J* 3 Hz, 8-H), and 8.10 (1 H, d, *J* 9 Hz, 11-H) (Found: M^+, 341.1332. $C_{19}H_{19}NO_5$ requires *M*, 341.1263); *m/z* 341 (6%), 325 (100), 324 (58), 308 (7), 307 (3), 305 (17), 295 (51), 294 (43), 282 (66), 281 (29), and 252 (31).

* Dibenzo[*de*,*g*]quinoline numbering scheme used.

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