Acta Chemica Scandinavica B 39 (1985) 867–875

Deidaclin and Tetraphyllin A, Epimeric Glucosides of 2-Cyclopentenone Cyanohydrin, in *Adenia globosa* ssp. *globosa* Engl. (Passifloraceae). Crystal Structure of Deidaclin Tetraacetate

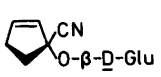
JERZY W. JAROSZEWSKI and BIRTHE JENSEN

Department of Chemistry BC, Royal Danish School of Pharmacy, Universitetsparken 2, DK-2100 Copenhagen, Denmark

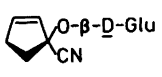
Deidaclin and tetraphyllin A, epimeric glucosides of 2-cyclopentenone cyanohydrin, co-occur in the passifloraceous plant *Adenia globosa* ssp. *globosa* Engl. Absolute configurations of the cyanohydrin centres of the glucosides were determined by low-temperature crystallographic study of deidaclin tetraacetate, established to be (*R*)-1-(tetra-*O*-acetyl-β-D-glucopyranosyloxy)-2-cyclopentenecarbonitrile. Co-occurrence of epimeric pairs of natural glucosides derived from 2-cyclopentenone cyanohydrin appears to be more common than hitherto known, and may be universal within this class of plant products.

Among natural cyanohydrin glycosides, those containing a cyclopentene ring in the aglycone portion, found in Passifloraceae, related tribes of Flacourtiaceae, and the neighbouring family Turneraceae, are still relatively poorly known. Unlike the classical cyanohydrins derived from protein amino acids,[1,2] the cyclopentenoids appear to arise from the non-protein amino acid 2-cyclopenteneglycine.[3] In this paper, we report on the isolation from *Adenia globosa* ssp. *globosa* Engl. (Passifloraceae) of epimeric glucosides of 2-cyclopentenone cyanohydrin, deidaclin (*1*) and tetraphyllin A (*2*), which are structural prototypes of all other compounds of this group. The epimers were isolated in pure form for the first time, the absolute configuration of the cyanohydrin centres being established by X-ray crystallographic investigation of the tetraacetate of deidaclin.

The glucosides of 2-cyclopentenone cyanohydrin were originally isolated more than a decade ago. Thus, *Deidamia clematoides* (C.H. Wright) Harms [now *Efulensia clematoides* C.H. Wright[4]] was shown to contain a glucoside, m.p. 128 °C, $[\alpha]_D^{27}$ −20.4° (*c* 1, water), named deidaclin,[3,5] whereas an apparently different compound, m.p. 118 °C, $[\alpha]_D^{25}$ −14.0° (*c* 1, water), was isolated from the New Zealand passion fruit *Tetrapathaea tetrandra* Cheeseman and named tetraphyllin A.[6,7] Subsequently, deidaclin was reported to occur in *Turnera ulmifolia* Linn. (Turneraceae).[8] However, the stereochemistry of the glucosides was never elucidated.



1



2

0302-4369/85 $2.50

Table 1. 270 MHz ^{1}H NMR spectra of epimeric β-D-glucopyranosides of 2-cyclopentenone cyanohydrin and their derivatives.

Compound	−CH=CH−	$-CH_2-CH_2-$	H1′ (anomeric)	H2′	H3′	H4′	H5′	H6′
Deidaclin [a]	5.96 and 6.27 [c]	2.4–2.65 (*m*)	4.61, $^3J_{1,2}$ 7.6 Hz	3.20 (*t* [d])	[e]	[e]	[e]	3.66(A) and 3.86(B); $^2J_{AB}$ −12.0, $^3J_{AX}$ 5.2, $^3J_{BX}$ 2.3 Hz
Tetraphyllin A [a]	6.00 and 6.34 [c]	2.5–2.6 (*m*)	4.52, $^3J_{1,2}$ 7.6 Hz	3.20 (*t* [d])	[e]	[e]	[e]	3.68(A) and 3.86(B); $^2J_{AB}$ −12.0, $^3J_{AX}$ 5.2, $^3J_{BX}$ 2.3 Hz
Deidaclin tetraacetate [b]	5.86 and 6.25 [c]	2.2–2.35 (*m*,1H) 2.4–2.65 (*m*,3H)	4.93, $^3J_{1,2}$ 7.8 Hz	5.01 (*dd*)	5.25 (*t* [f])	5.04 (*t* [f])	3.79 (*dq*)	4.16(A) and 4.22(B); $^2J_{AB}$ −12.2, $^3J_{AX}$ 2.7, $^3J_{BX}$ 5.6 Hz
Tetraphyllin A tetraacetate [b]	5.83 and 6.30 [c]	2.35–2.65 (*m*)	4.86, $^3J_{1,2}$ 7.8 Hz	5.00 (*dd*)	5.24 (*t* [f])	5.06 (*t* [f])	3.79 (*dq*)	4.17(A) and 4.26(B); $^2J_{AB}$ −12.2, $^3J_{AX}$ 2.7, $^3J_{BX}$ 5.6 Hz
Tetra-*O*-trimethylsilyldeidaclin [b]	6.05 and 6.15 [c]	2.3–2.7 (*m*)	4.63, $^3J_{1,2}$ 7.3 Hz	[g]	[g]	[g]	[g]	3.60(A) and 3.80(B); $^2J_{AB}$ −11.0, $^3J_{AX}$ 6.3, $^3J_{BX}$ 2.2 Hz
Tetra-*O*-trimethylsilyltetraphyllin A [b]	5.88 and 6.25 [c]	2.4–2.6 (*m*)	4.53, $^3J_{1,2}$ 7.3 Hz	[g]	[g]	[g]	[g]	3.65(A) and 3.80(B); $^2J_{AB}$ −11.0, $^3J_{AX}$ 5.5 Hz, $^3J_{BX}$ 2.2 Hz

[a] In methanol-d_4. [b] In chloroform-*d*. [c] Doublet of triplets; $^3J_{AB}$ 5.6 Hz, $^3J_{AX} \sim {}^3J_{AY} \sim {}^4J_{BX} \sim {}^4J_{BY} \sim 2.3$ Hz (absolute values). [d] Identified by decoupling of H1′. [e] Complex pattern at δ 3.3–3.45. [f] The two triplets were distinguished by decoupling of H5′; $^3J_{2,3} \sim {}^3J_{3,4} \sim {}^3J_{4,5} \sim 9.3$ Hz. [g] Complex pattern at δ 3.2–3.5.

Table 2. 67.9 MHz ^{13}C NMR spectra of epimeric β-D-glucopyranosides of 2-cyclopentenone cyanohydrin and their derivatives.

Compound	C1	C2, C3	C4, C5	CN	C1′ (anomeric)	Remaining glucose carbons
Deidaclin [a]	84.9	131.0, 140.7	31.6, 38.5	120.6	101.4	62.5, 71.3, 74.7, 77.9, 78.1
Tetraphyllin A [a]	84.1	129.9, 141.9	32.0, 39.2	121.0	100.9	62.6, 71.4, 74.8, 78.0, 78.1
Deidaclin tetraacetate [b,c]	83.9	129.1, 140.1	30.6, 37.7	118.4	98.0	62.0, 68.4, 71.0, 72.3, 72.7
Tetraphyllin A tetraacetate [b,d]	83.3	128.5, 141.0	31.2, 37.7	118.4	97.8	61.9, 68.4, 71.1, 72.3, 72.7
Tetra-*O*-trimethyl-silyl-deidaclin [b]	83.7	130.8, 138.3	30.4, 37.6	119.0	100.5	62.2, 71.7, 75.2, 77.0, 78.2
Tetra-*O*-trimethyl silyl-tetraphyllin A [b]	83.6	130.7, 138.3	30.4, 37.5	118.9	100.4	62.1, 71.6, 75.2, 77.0, 78.2

[a] In methanol-d_4. [b] In chloroform-*d*. [c] Acetyl groups: δ 20.6 (4 CH_3), 169.2, 169.4, 170.0, 170.4 (CO). [d] Acetyl groups: δ 20.6 (4 CH_3), 169.1, 169.4, 170.1, 170.6 (CO).

The genus *Adenia* Forsk.[9] consists of nearly 100 species, some of which have previously been reported to be cyanogenic.[5] Cyclopentenoids in which the ring is hydroxylated at the allylic position have recently been isolated from *Adenia digitata* (Harv.) Engl.,[10] *A. glauca* Schinz,[11] and *A. volkensii* Harms.[12]

RESULTS AND DISCUSSION

A. globosa Engl. is a thorny climber growing in scrub savannah of tropical East Africa.[9] Three allopatric subspecies are recognized; the material used in this work was *A. globosa* ssp. *globosa*. Extraction of freeze-dried plant material with boiling 80 % aqueous methanol and repeated fractionation of the crude extract on silica gel in two solvent systems, followed by preparative HPLC on octadecylsilyl silica, afforded an apparently homogeneous cyanogenic fraction, which, however, could be separated into two components in the ratio of 4:1 by normal-phase preparative HPLC.

Table 3. Fractional atomic coordinates and equivalent isotropic thermal parameters (10^2 Å^2) of non-hydrogen atoms of deidaclin tetraacetate. $U_{eq}=\frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\boldsymbol{a}_j$.

Atom	*x*	*y*	*z*	U_{eq}
C1	0.4917(1)	0.4693(6)	0.3096(2)	1.6
C2	0.4801(1)	0.6676(6)	0.3481(2)	1.8
C3	0.5300(2)	0.7164(6)	0.4115(2)	2.1
C4	0.5811(2)	0.5624(8)	0.4305(2)	2.6
C5	0.5490(2)	0.3841(7)	0.3783(2)	2.4
C11	0.5091(2)	0.4999(6)	0.2207(2)	2.2
N	0.5231(2)	0.5212(7)	0.1531(2)	3.4
O1	0.4394(1)	0.3298(5)	0.2990(1)	1.6
C1′	0.3801(1)	0.3987(–)	0.2530(2)	1.3
C2′	0.3414(1)	0.2225(6)	0.2103(2)	1.4
C3′	0.2712(1)	0.2808(6)	0.1736(2)	1.4
C4′	0.2423(1)	0.3944(6)	0.2419(2)	1.2
C5′	0.2868(1)	0.5676(6)	0.2760(2)	1.4
O5′	0.3477(1)	0.4849(5)	0.3164(1)	1.4
O2′	0.3697(1)	0.1640(5)	0.1359(1)	1.5
C2′1	0.3864(1)	−0.0275(6)	0.1295(2)	1.4
O2′1	0.3802(1)	−0.1496(5)	0.1835(2)	2.3
C2′2	0.4117(1)	−0.0604(6)	0.0456(2)	2.0
O3′	0.2333(1)	0.1054(5)	0.1535(1)	1.6
C3′1	0.2073(1)	0.0668(6)	0.0669(2)	1.6
O3′1	0.2204(1)	0.1594(6)	0.0054(2)	2.6
C3′2	0.1615(2)	−0.1011(7)	0.0603(2)	2.4
O4′	0.1793(1)	0.4592(5)	0.1961(1)	1.6
C4′1	0.1310(1)	0.4576(6)	0.2439(2)	1.8
O4′1	0.1402(1)	0.4227(6)	0.3224(2)	2.5
C4′2	0.0672(2)	0.5060(7)	0.1858(2)	2.2
C6′	0.2622(1)	0.6849(6)	0.3463(2)	1.7
O6′	0.3093(1)	0.8379(5)	0.3744(1)	1.7
C6′1	0.2916(1)	0.9695(6)	0.4300(2)	1.4
O6′1	0.2383(1)	0.9722(6)	0.4486(2)	2.7
C6′2	0.3453(1)	1.1072(6)	0.4664(2)	1.8

Investigation of the crystalline compounds thus obtained by ^{1}H and ^{13}C NMR spectroscopy revealed both to be β-glucopyranosides of 2-cyclopentenone cyanohydrin. The compounds must therefore differ in chirality at the cyanohydrin centre. The sugar set free on enzymatic hydrolysis of the compounds was confirmed to be *D*-glucose using the glucose oxidase test.

The spectroscopic data for deidaclin and tetraphyllin A published in the literature [3,6,13–15] are largely fragmentary. A direct comparison between the glucosides isolated in the present work and authentic deidaclin and tetraphyllin A was therefore carried out. A sample [5] of the former was obtained through the kindness of Dr. Lucie H. Fikenscher, Leiden, Holland. According to spectroscopic and chromatographic properties, authentic deidaclin was identical with the major glucoside of *A. globosa* ssp. *globosa.* The minor glucoside was identical with authentic tetraphyllin A, reisolated [16] from *T. tetrandra.* Thus, *A. globosa* ssp. *globosa* contains deidaclin and tetraphyllin A in ratio of 4:1. A summary of ^{1}H and ^{13}C NMR spectroscopic properties of the glucosides and their derivatives is given in Tables 1 and 2.

The remaining issue is the absolute configuration of the cyanohydrin centres of the glucosides. Unlike deidaclin, which had a pronounced tendency to form twin crystals, its tetraacetate gave well-shaped crystals suitable for X-ray diffractometry. Refinement of the structure to $R=0.046$ for 3353 independent reflections allowed unambiguous identification of all hydrogen atoms (apart from the disorder exhibited by the hydrogens of the 6-*O*-acetyl group) as well as of the short C=C distance in the cyclopentene ring (cf. Tables 3 and 4), revealing the configuration of the cyanohydrin centre to be (*R*) (*1*). An ORTEP [17] drawing of the molecule is shown in Fig. 1. Consequently, the configuration of the corresponding centre of tetraphyllin A is (*S*) (*2*).

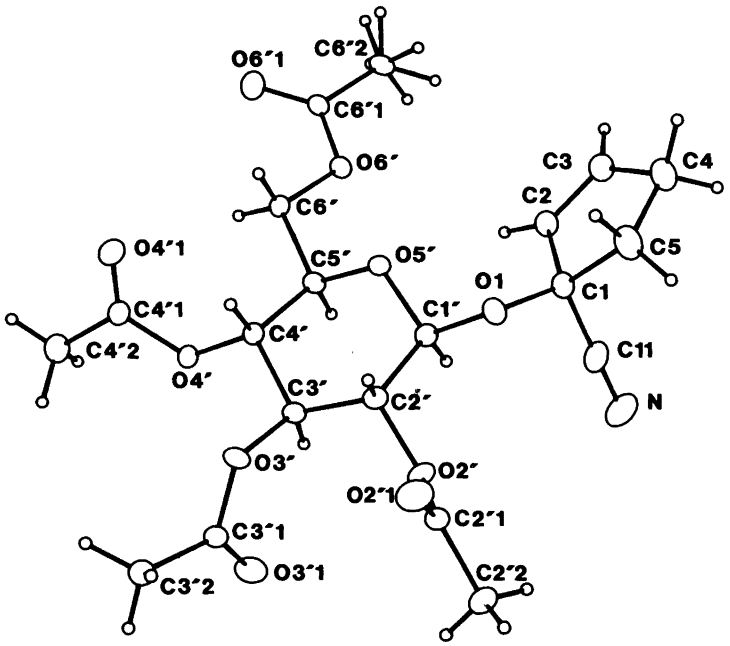


Fig. 1. Drawing of the molecule of deidaclin tetraacetate showing the numbering system of the atoms. Thermal ellipsoids enclose regions of 50 % probability, while hydrogen atoms are represented by spheres with radii of 0.07 Å.

Table 4. Selected bond lengths (Å), valence angles and torsion angles (deg).

O1–C1	1.441(4)	C1–C2–C3	110.1(3)
C1–C2	1.515(6)	C2–C3–C4	113.9(4)
C2–C3	1.329(4)	C3–C4–C5	103.1(3)
C3–C4	1.492(6)	C4–C5–C1	105.2(3)
C4–C5	1.540(6)	C5–C1–C2	103.5(3)
C5–C1	1.553(4)	C1–C11–N	179.1(6)
C1–C11	1.492(5)	C1′–C2′–C3′	110.5(3)
C11–N	1.140(5)	C2′–C3′–C4′	111.5(2)
O1–C1′	1.393(3)	C3′–C4′–C5′	109.2(2)
C1′–C2′	1.527(4)	C4′–C5′–O5′	106.3(3)
C2′–C3′	1.530(4)	C5′–O5′–C1′	112.1(2)
C3′–C4′	1.521(5)	O5′–C1′–C2′	109.5(2)
C4′–C5′	1.536(5)	C2′–C1′–O1	107.6(2)
C5′–O5′	1.430(4)	O5′–C1′–O1	107.2(2)
O5′–C1′	1.418(4)	C1–O1–C1′	115.2(3)
C5′–C6′	1.511(5)		

C1–C2–C3–C4	– 2.9(4)
C2–C3–C4–C5	–10.1(4)
C3–C4–C5–C1	18.2(4)
C4–C5–C1–C2	–19.9(3)
C5–C1–C2–C3	14.5(4)
C1–O1–C1′–O5′	–88.6(3)
O1–C1′–O5′–C5′	177.9(3)
C1′–C2′–C3′–C4′	–48.8(4)
C2′–C3′–C4′–C5′	53.1(4)
C3′–C4′–C5′–O5′	–60.9(3)
C4′–C5′–O5′–C1′	69.1(3)
C5′–O5′–C1′–C2′	–65.6(3)
O5′–C1′–C2′–C3′	53.1(3)

The tetra-*O*-acetylglucopyranose moiety of the glucoside adopts the usual $^4C_1$ conformation, with bond lengths and angles similar to those of methyl tetra-*O*-acetyl-β-D-glucopyranoside[18] and the average pyranose structure.[19,20] The glucosidic bond (C1′–O1) shows the familiar anomeric shortening by 0.025 Å as compared to the O5′–C1′ bond. The O1–C1′–O5′–C5′ torsion angle of 178° is normal;[21] the C1–O1–C1′–O5′ torsion angle is –89°, somewhat larger than in methyl β-D-aldopyranosides, but typical of glucosides with bulky aglycones.[21] The cyclopentene ring forms an envelope,[22] with C5 placed 0.32 Å away from the best plane through the remaining four carbon atoms.

Finally, we report that our sample of authentic deidaclin from *E. clematoides*[5] contained about 10 % of tetraphyllin A (^{1}H and ^{13}C NMR, HPLC). The occurrence of pairs of cyclopentenoid cyanohydrin glucosides differing in configuration of the cyanohydrin centres has previously been reported in several cases;[7,11,12,23] in one additional instance[8] the ^{1}H NMR spectrum reproduced in the literature suggests co-occurrence of the epimers, too. The occurrence in plants of epimeric pairs of cyclopentenoid cyanohydrin glucosides is thus a characteristic phenomenon, only extremely rarely[24,25] encountered with other types of natural cyanohydrins. The phenomenon may actually be universal within this type of natural products, and we suggest that in cases where only one epimer appears to be present, the co-occurrence of the second epimer should not be dismissed unless the isolate was carefully

scrutinized by refined techniques. The epimers of cyclopentenoid glycosides, not resolvable or only poorly resolvable by reversed-phase HPLC,[16] may well be easily separated by HPLC on unmodified silica, as demonstrated in this work for *1* and *2*. The enzymatic control mechanisms underlying the production of the epimeric pairs have yet to be elucidated, but the formation of the epimers may be plainly related to the ability of plants to synthesize both diastereoisomers of L-2-cyclopenteneglycine, which were actually demonstrated to be present in some Flacourtiaceae.[26]

EXPERIMENTAL

General. Plant material used in this work was collected in a greenhouse of the Botanical Garden, University of Copenhagen, Copenhagen. NMR and IR spectra were obtained on a Bruker HX-270 spectrometer and on a Perkin Elmer model 781 spectrophotometer, respectively. Optical rotations were measured with a Perkin Elmer model 141 polarimeter. Melting points were determined in capillaries and are corrected. Column chromatography and thin-layer chromatography were carried out using Merck Kieselgel 60, 0.066–0.2 mm, and Merck Kieselgel 60 plates, respectively. HPLC separations were carried out with a chromatograph consisting of a Waters model 6000A pump, Rheodyne model 7125 injector (2 ml loop), Knauer UV/RI detector and a recorder, using 1.6×20 cm Knauer columns.

Isolation of the glucosides. Freshly collected plant material was frozen with liquid nitrogen and freeze-dried. Finely pulverized, dry material (39 g) was dropped in small portions into 400 ml of boiling aqueous methanol (80 vol. %), boiled for 3–4 min, chilled, and filtered, the filter cake being repeatedly washed with boiling solvent. The combined extracts were evaporated almost to dryness, the residue suspended in methanol, *ca.* 25 g of silica gel added, and the mixture evaporated to dryness *in vacuo*. The resulting powder was applied on top of a 2.5×75 cm column of silica gel, and the column eluted with ethyl acetate/acetone/methanol 4:4:1 (v/v).

The fractions were monitored by TLC with the same solvent, using a sugar-specific (naphthoresorcinol reagent[27]) as well as a cyanide-specific (sandwich picrate assay[28]) method of visualizing the spots. The cyanogenic fractions were evaporated and the residue (1.8 g) chromatographed again as described above, but using ethyl acetate/methanol/water 93:5:2 (v/v) as the eluant, to give 400 mg of the crude cyanogenic constituent. Further purification was carried out by preparative HPLC on Lichrosorb RP-18, 10 μm, using water/methanol 7:3 (v/v) at a rate of 5 ml/min. The mixture of *1* and *2* was eluted as a single peak with $k'=3.5$. The yield was 250 mg or 0.64 % of dry weight. The mixture was resolved by HPLC on Lichrosorb Si60, 7 μm, with 5 ml/min of ethyl acetate/methanol/water 93:5:2 (v/v). In this system, deidaclin was eluted before tetraphyllin A, the separation factor being 1.09 (the column had 9000 theoretical plates). The glucosides were finally crystallized from ethyl acetate.

Deidaclin: m.p. 129–130 °C, lit.[5] m.p. 127–128 °C; $[\alpha]_D^{26}$ −25° (*c* 1.1, 96 % ethanol), lit.[3,5] $[\alpha]_D^{27}$ −20.4° (*c* 1, water), $[\alpha]_D^{24}$ −23.6° (*c* 1, ethanol); IR (KBr): 1620 (w), 3200–3600 (s) cm^{-1}.

Tetraphyllin A: m.p. 119–120 °C, lit.[6] m.p. 116–118 °C; $[\alpha]_D^{26}$ −20° (*c* 0.4, 96 % ethanol), lit.[6] $[\alpha]_D^{25}$ −14° (*c* 1, water); IR (KBr): 1625 (w), 3200–3600 (s) cm^{-1}.

Enzymatic[28] hydrolysis of the crystalline glucosides yielded D-glucose, as shown by use of the D-glucose oxidase test (Clinistix Paper, Ames Company).

Preparation of derivatives. The acetates of *1* and *2* were obtained in practically quantitative yield by overnight treatment with a 1:1 mixture of acetic anhydride and pyridine at 20 °C, evaporation and recrystallization of the residues from ether–light petroleum.

Deidaclin tetraacetate: m.p. 131–132 °C, IR (KBr): 1620 (w), 1750 (s) cm^{-1}. Anal. $C_{20}H_{25}NO_{10}$: C,H,N.

Tetraphyllin A tetraacetate: m.p. 108–110 °C, lit.[6] m.p. 108–109 °C, IR (KBr): 1620 (w), 1750 (s) cm^{-1}.

The per-*O*-trimethylsilyl derivatives of the glucosides were obtained by heating during 20 min at 40 °C with a 1:1:1 mixture of trimethylsilyl chloride, hexamethyldisilazane and pyridine, followed by evaporation.

Crystal structure determination. Deidaclin tetraacetate, $C_{20}H_{25}NO_{10}$. M=439.42. Space group $C2$, a=21.057(7), b=6.827(3), c=15.321(5) Å, β=101.11(2)°, V=2161(2) Å^3, Z=4, D_c=1.35 g cm^{-3}. *T ca.* 100 K, μ(Mo$K\alpha$)=0.102 mm^{-1}. F(000)=928. The unit cell parameters were refined by leastsquares techniques from the angles measured for 21 reflections on the NONIUS CAD-4 diffractometer used for data collection. Intensity data were collected from a crystal with dimensions less than 0.3 mm, cooled by means of liquid nitrogen in order to avoid evaporation of the crystal and to improve diffraction. Of 5936 reflections measured ($\theta \leq 35°$) 4734 were independent, of which 3353 had $I_{net} > 2.0\sigma(I)$, where σ is the standard deviation from counting statistics. No correction for absorption was used.

The structure was solved by use of MULTAN 80,[29] and refined to a final R value of 0.046 with the programs of the X-RAY System.[30] All hydrogen atoms could be located in a difference electron-density map; those connected to C6′2 exhibited disorder and were introduced and kept fixed as six atoms with occupancy factors 0.5. The refinement included positional and thermal parameters for all atoms except the H-atoms connected to C6′2. Thermal parameters for non-hydrogen atoms were anisotropic, those of H-atoms were isotropic. The quantity minimized was $\Sigma w(|F_o|-|F_c|)^2$, where $w=(4.0+F_o+0.025F_o^2+0.0005F_o^3)^{-1}$. The X-ray atomic scattering factors used for H-atoms were those of Stewart, Davidson and Simpson, [31] and for the other atoms those listed in International Tables for X-Ray Crystallography.[32]

Supplementary material including lists of final structure factors, parameters of H-atoms and anisotropic temperature factors (10 pages) can be obtained from RECKU, Vermundsgade 5, DK-2100 Copenhagen, Denmark, under code DANDOK/0002/85. The material will be sent in photocopy free of charge.

Acknowledgements. We thank Drs. F. Arnklit, J. Damgaard, and K. Rahn, Botanical Garden, University of Copenhagen, for supplying and identifying *A. globosa* ssp. *globosa,* Dr. E. Edgar, Botany Division, Department of Scientific and Industrial Research, Christchurch, New Zealand, for supplying *T. tetrandra,* Dr. L.H. Fikenscher, Laboratory of Experimental Plant Systematics, Leiden, Holland, for authentic deidaclin, Dr. K. Schaumburg, Department of Chemical Physics, University of Copenhagen, for access to NMR facilities, Dr. M.G. Ettlinger, Department of General and Organic Chemistry, University of Copenhagen, for valuable comments, and Mr. F. Hansen, Department of Physical Chemistry, University of Copenhagen, for collecting the crystallographic data. The X-ray and NMR equipment used in this work was purchased by the Danish Natural Science Research Council.

REFERENCES

1. Seigler, D.S. In Vennesland, B., Conn, E.E., Knowles, C.J., Westley, J. and Wissing, F., Eds., *Cyanide in Biology,* Academic, London 1981, p.133.
2. Conn, E.E. In Akazawa, T., Asahi, T. and Imaseki, H., Eds., *The New Frontiers in Plant Biochemistry,* Japan Scientific Societies Press, Tokyo 1983, p. 11.
3. Clapp, R.C., Ettlinger, M.G. and Long, L., Jr. *J. Am. Chem. Soc. 92* (1970) 6378.
4. De Wilde, W.J.J.O. *Blumea 22* (1974) 31.
5. Tantisewie, B., Ruijgrok, H.W.L. and Hegnauer, R. *Pharm. Weekblad 104* (1969) 1341.
6. Russell, G.B. and Reay, P.F. *Phytochemistry 10* (1971) 1373.
7. Spencer, K.C., Seigler, D.S. and Domingo, J.L. *Phytochemistry 22* (1983) 1815.
8. Spencer, K.C. and Seigler, D.S. *Phytochemistry 19* (1980) 1863.
9. De Wilde, W.J.J.O. *A Monograph of the Genus* Adenia *Forsk.* (*Passifloraceae*), H. Veenman & Zonen, N.V., Wageningen 1971.
10. Spencer, K.C. and Seigler, D.S. *Phytochemistry 21* (1982) 653.
11. Spencer, K.C. and Seigler, D.S. *Onderstepoort J. Vet. Res. 49* (1982) 137.
12. Gondwe, A.T.D., Seigler, D.S. and Dunn, J.E. *Phytochemistry 17* (1978) 271.
13. Seigler, D.S. *Phytochemistry 14* (1975) 9.
14. Seigler, D.S. *Progr. Phytochem. 4* (1977) 83.
15. Hübel, W., Nahrstedt, A. and Wray, V. *Arch. Pharm. (Weinheim) 314* (1981) 609.

16. Jaroszewski, J.W. *Unpublished work.*
17. Johnson, C.K. *ORTEP II*: Report ORNL-3794, revised. Oak Ridge National Laboratory, Oak Ridge 1971.
18. Zugenmaier, P. and Rappenecker, G. *Acta Crystallogr. B 34* (1978) 164.
19. Arnott, S. and Scott, W.E. *J. Chem. Soc. Perkin Trans. 2* (1972) 324.
20. Sheldrick, B. and Akrigg, D. *Acta Crystallogr. B 36* (1980) 1615.
21. Pérez, S. and Marchessault, R.H. *Carbohydr. Res. 65* (1978) 114.
22. Saebo, S., Cordell, F.R. and Boggs, J.E. *Theochem. J. Mol. Struct. 13* (1983) 221.
23. Seigler, D.S., Spencer, K.C., Statler, W.S., Conn, E.E. and Dunn, J.E. *Phytochemistry 21* (1982) 2277.
24. Jensen, S.R. and Nielsen, B.J. *Acta Chem. Scand. 27* (1973) 2661.
25. Brimer, L. and Dalgaard, L. *J. Chromatogr. 303* (1984) 77.
26. Cramer, U., Rehfeldt, A.G. and Spener, F. *Biochemistry 19* (1980) 3074.
27. Stahl, E. *Dünnschicht-Chromatographie; Ein Laboratoriumshandbuch,* Springer, Berlin 1967, p. 840.
28. Brimer, L., Christensen, S.B., Mølgaard, P. and Nartey, F. *J. Agric. Food. Chem. 31* (1983) 789.
29. Main, P., Fiske, S.J., Hull, S.E., Lessinger, L., Germain, G., Declecq, J.-P. and Woolfson, M.M. *MULTAN 80: A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data,* Universities of York, England and Louvain, Belgium 1980.
30. Stewart, J.M., Machin, P.A., Dickinson, C.W., Anramon, H.L., Heck, H. and Flack, H. *The X-Ray System,* Technical Report TR-446, Computer Science Center, University of Maryland, College Park 1976.
31. Stewart, R.F., Davidson, E.R. and Simpson, W.T. *J. Chem. Phys. 42* (1965) 3175.
32. *International Tables for X-Ray Crystallography,* Kynoch Press, Birmingham 1974, Vol. 4.

Received February 18, 1985.