Phytochemistry, Vol. 22, No. 3, pp. 749–753, 1983.
Printed in Great Britain.

0031–9422/83/030749–05$03.00/0

LIGNANS AND OTHER CONSTITUENTS FROM *CARISSA EDULIS**

HANS ACHENBACH, REINER WAIBEL and IVAN ADDAE-MENSAH†

Department of Pharmaceutical Chemistry, Institute of Pharmacy, University Erlangen-Nürnberg, West Germany; †Chemistry Department, University of Ghana, Legon, Ghana

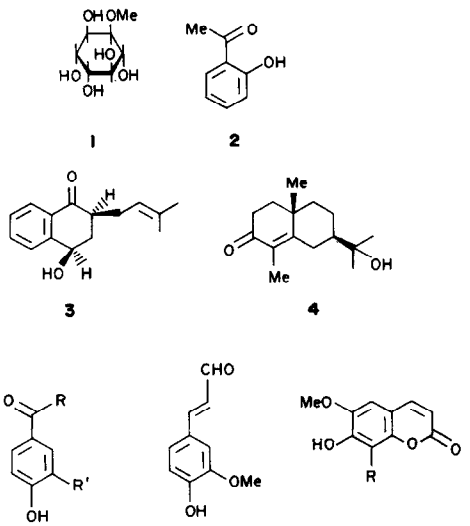
(*Received* 22 *June* 1982)

Key Word Index—*Carissa edulis*; Apocynaceae; lignans; lignan carissanol; carisson; aromatic compounds; 4-hydroxy-(3-hydroxypropionyl)-benzene.

Abstract—The methanolic extract from the root of *Carissa edulis* contains *ca* 5% lignans, the main compounds among them being (−)-nortrachelogenin, carinol and the hitherto unknown carissanol.

INTRODUCTION

Various plants of the genus *Carissa* are used in India and other regions of Asia as medicinal agents. [1]. In West Africa, the root of *C. edulis* is reported as a remedy against various diseases [2, 3]. The presence of cardioactive substances has been demonstrated in some Asian *Carissa* species [4, 5] and in consequence the Indian *C. carandas* has been studied phytochemically in more detail [6–10]. Very little is known about the constituents of *C. edulis*: a French group isolated the inosit derivative quebrachitol (**1**) from the twigs [11] and, in a general screening test for digitalis-type glycosides, extracts were found to be negative [12].



1 2 3 4

5 R=H, R'=OMe
6 R=CH$_2$–CH$_2$OH, R'=H
7
8 R=H
9 R=OMe

* Part 12 in the series "Constituents of West African Medicinal Plants". For Part 11 see, Achenbach, H., *Rev. Latinoam. Quim.* (in press).

RESULTS AND DISCUSSION

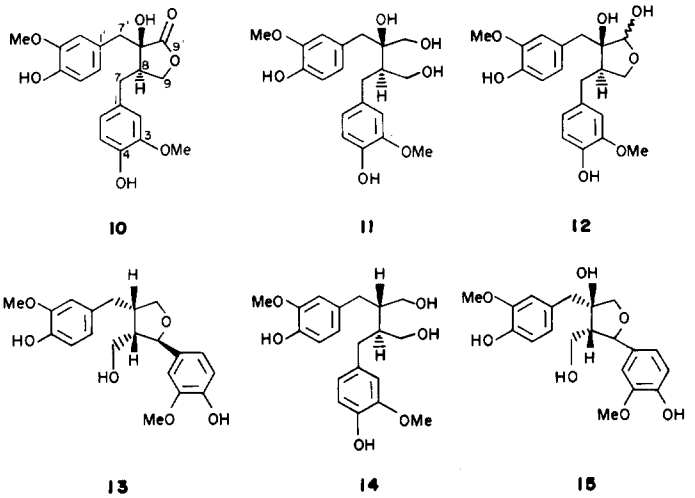
The methanolic extract from the root of *C. edulis* was concentrated and partitioned between (a) petrol, (b) tetrachloromethane, (c) diethyl ether, (d) ethyl acetate and (e) water. The petrol phase contained a mixture of pentacyclic triterpenes and *o*-hydroxyacetophenone (**2**); in the tetrachloromethane phase we found traces of catalponol (**3**) [13, 14] and a mixture of sesquiterpenes, mainly carisson (**4**), which was first isolated from *C. lanceolata* in 1954 [15] and later in two other *Carissa* species [1, 16]. Chromatography of the ether phase on Si gel yielded, besides small amounts of the aromatic compounds **5–9**, a mixture of lignans (90% of the ether phase) which were further separated chromatographically into the three major lignans **10–12** and the three minor lignans **13–15**.

Compounds **10** and **11** were identified, on the basis of their physicochemical data and the spectra of their acetylation products, as (−)-nortrachelogenin (**10**) [17, 18] and carinol (**11**) [19], respectively.

The structure of **12** was deduced from its ^{1}H, ^{13}C NMR and mass spectra and the corresponding spectra of its acetyl derivatives. In agreement with the lactol group in **12** are the observations that **12** (a) in solution exists, according to ^{1}H and ^{13}C NMR spectra, as a mixture of epimers, (b) forms two epimeric *O*-alkyl derivatives on treatment with alcohol–H$^+$, and (c) is converted into **11** by reduction with lithium aluminium hydride in diethyl ether. On the other hand **12**, as well as **11**, can be prepared by careful reduction of **10** with lithium aluminium hydride in tetrahydrofuran. This latter reaction also determines the absolute configuration of **12**.

In the same manner as for **10** and **11**, the structures of the minor lignans were identified as the already known compounds (+)-lariciresinol (**13**) [20], (−)-secoisolariciresinol (**14**) [21] and (−)-olivil (**15**) [20].

The lignans altogether constitute *ca* 5% of the total methanolic extract and the three major compounds **10–12** *ca* 1% each. Compound **12** represents a new lignan of the comparatively rare lactol-type; it consequently was named carissanol. (−)-Nortrachelogenin has been found only once as a constituent of *Trachelospermum asiaticum* (Apocynaceae), a plant used in China against various diseases [24]. (+)-Nortrachelogenin, the enantiomer of



10 11 12

13 14 15

10, which was isolated from some *Wikstroemia* species (Thymelaeaceae) [25, 26, 28] has been proved to possess antitumor activity [26]. Up to now, no biological activities have been reported for (−)-nortrachelogenin (**10**) or carinol (**11**).

EXPERIMENTAL

General procedures. If not stated otherwise, all general procedures and instruments were as described in ref. [22]. MS were run at 70 eV. For TLC we used 0.25 mm Si gel N/UV_{254} (Macherey-Nagel) and the solvent system $CHCl_3$–MeOH (9:1); detection by UV at 254 nm and by anisaldehyde reagent No. 15 according to Stahl [23].

Plant material. Roots of *C. edulis* Vahl were collected near Legon, Ghana, in March 1979 and identified by Mr. A. A. Enti. A herbarium specimen is deposited in our collection under No. 79/1.

Extraction procedure. Powdered dried roots (2.5 kg) were extracted with 15 l. MeOH in a Soxhlet apparatus. On evaporation this extract yielded 155 g residue, which was redissolved in 3 l. MeOH–H_2O (1:1) and then treated successively with 8 × 250 ml petrol (upon evaporation: 35 g extract A), 8 × 250 ml CCl_4 (8 g extract B), 20 × 250 ml Et_2O (11 g extract C) and 20 × 500 ml EtOAc (13 g extract D).

Extract A was separated over 300 g Si gel (column operated at *ca* 30 psi) into eight fractions (A1–A8) using cyclohexane with increasing amounts of EtOAc as eluent.

o-Hydroxyacetophenone (**2**). Rechromatography of A3 over 250 g Si gel with petrol–Me_2CO (19:1) gave 1.2 g **2**.

Catalponol (**3**). Extract B contained mainly carisson (**4**) and other sesquiterpenes. Besides these, repeated chromatography over Si gel with different solvent systems afforded *ca* 4 mg of a viscous oil, $[\alpha]_D^{20}$ + 16° ($CHCl_3$; *c* 0.31), physicochemical data identical with **3** [13, 14]. Extract C was separated over 200 g Si gel (column operated at *ca* 30 psi) into five fractions (C1–C5) using $CHCl_3$ with increasing amounts of MeOH as eluent. C1 by rechromatography over 250 g Sephadex LH 20 with MeOH–$CHCl_3$ (7:3) gave three fractions (C1.1–C1.3). C1.2 was further separated over 160 g Si gel (petrol–EtOAc, 3:2) into nine fractions (C1.2.1–C1.2.9).

Vanillin (**5**) *and coniferaldehyde* (**7**). On evaporation, from C1.2.4 crystallized 10 mg **5** and from C1.2.5 14 mg **7**.

(−)-*Nortrachelogenin* (**10**). On evaporation, C1.2.7 afforded 275 mg of an amorphous powder, $[\alpha]_D^{20}$ − 25° (EtOH; *c* 1.5), physicochemical data identical with **10** [17, 18]; ^{13}C NMR: Table 2.

Scopoletin (**8**). Purification of C1.3 over 6 g Si gel (toluene–MeOH, 19:1) yielded 3 mg **8** [29].

Isofraxidin (**9**). Rechromatography of C2 over 60 g Si gel ($CHCl_3$–EtOAc, 3:2) gave 6.5 mg **9** [27].

C3 was separated over 400 g Si gel using $CHCl_3$–EtOAc (1:1) into four fractions (C3.1–C3.4). Further chromatography of C3.2 over 5 g Si gel using $CHCl_3$–EtOAc–MeOH (5:4:1) gave three fractions (C3.2.1–C3.2.3).

4-Hydroxy-(3-hydroxypropionyl)-benzene (**6**). Evaporation of C3.2.1 yielded 1.5 mg **6** as a colourless powder; MS: *m/z* (int. ≥ 5%) 166.0638 $C_9H_{10}O_3$ (18, M^+), 148 (6), 123 (11), 122 (8), 121 (100), 93 (21), 65 (14); UV λ_{max}^{EtOH} nm (log ε): 220 (4.15), 273sh, 279 (4.32); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3520, 1602; ^1H NMR (Me_2CO-d_6): δ 9.22 ($1H_{ex}$, *s*, ar-OH), 7.93 and 6.93 (4H, AA'BB', ar-H), 3.92 (2H, *dt*, $J_1 \approx J_2 \approx 6$ Hz, CH_2–CH_2–OH), 3.60 ($1H_{ex}$, *t*, $J = 6$ Hz, OH), 3.14 (2H, *t*, $J = 6$ Hz, CO–CH_2–CH_2–OH).

(+)-*Lariciresinol* (**13**). On concn, C3.2.3 gave 2 mg colourless crystals [mp 166–169°, $[\alpha]_D^{20}$ + 10° (EtOH; *c* 0.2)], data identical with **13** [20]; acetylation (Ac_2O–pyridine) converted **13** into the triacetyl derivative, whose spectra were identical with published data [30].

Carissanol (**12**). Rechromatography of C3.4 over 150 g Si gel with the lower phase of $CHCl_3$–MeOH–H_2O (18:1:1) afforded 250 mg **12** as an amorphous powder; $[\alpha]_D^{20}$ − 14° (EtOH; *c* 0.7); $C_{20}H_{24}O_7$ (376.4). (Found: C, 63.92; H, 6.26. Calc.: C, 63.82; H, 6.43%.) MS: *m/z* (int. ≥ 5%) 376.1538 $C_{20}H_{24}O_7$ (9, M^+), 193 (8), 175 (8), 164 (5), 163 (13), 150 (5), 139 (6), 138 (36), 137 (100), 131 (8), 124 (7), 123 (7), 122 (11), 107 (5), 94 (9), 91 (5), 77 (9), 65 (6), 55 (11), 51 (7); UV λ_{max}^{EtOH} nm (log ε): 228 (4.05), 282 (3.72); IR ν_{max}^{KBr} cm^{-1}: 3430, 1605, 1515; ^1H NMR: Table 1; ^{13}C NMR: Table 2.

C4 was separated over 250 g Sephadex LH 20 with MeOH–$CHCl_3$ (7:3) into five fractions (C4.1–C4.5).

(−)-*Secoisolariciresinol* (**14**). Rechromatography of C4.3 over 60 g Si gel using $CHCl_3$–MeOH–EtOAc (45:2:3) gave five fractions (C4.3.1–C4.3.5). C4.3.3, upon purification over 10 g Si gel (toluene–MeOH, 9:1), afforded 10 mg crystals [mp 113–114°, $[\alpha]_D^{20}$ − 28° (EtOH; *c* 0.33)] physicochemical data identical with **14** [21].

(−)-*Olivil* (**15**). Repeated chromatography of C4.4 over firstly 60 g Si gel ($CHCl_3$–MeOH–EtOAc, 45:2:3) and then 3 g Si gel ($CHCl_3$–MeOH, 19:1) gave 4 mg colourless crystals

Table 1. ^{1}H NMR data of lignans (in acetone-d_6)

	10	11	12	13	14	15
H-2	6.79 (*d*, J = 2)	6.85 (*d*, J = 2)	7.07–6.57	6.95 (*d*, J = 2)	6.74 (2H, *d*, J = 2)	7.14 (*d*, J = 2)
H-2′	6.83 (*d*, J = 2)	7.01 (*d*, J = 2)		6.84 (*d*, J = 2)		6.96 (*d*, J = 2)
H-5	6.76 (*d*, J = 8)	6.8–6.07*		6.80 (*d*, J = 8)	6.71 (2H, *d*, J = 8)	6.73 (*d*, J = 8)
H-5′	6.77 (*d*, J = 8)			6.75 (*d*, J = 8)		6.75 (*d*, J = 8)
H-6	6.66 (*dd*, J_1 = 8, J_2 = 2)	6.82 (*dd*, J_1 = 8, J_2 = 2)		6.75 (*dd*, J_1 = 8, J_2 = 2)	6.61 (2H, *dd*, J_1 = 8, J_2 = 2)	6.88 (*dd*, J_1 = 8, J_2 = 2)
H-6′	6.70 (*dd*, J_1 = 8, J_2 = 2)	6.71 (*dd*, J_1 = 8, J_2 = 2)		6.66 (*dd*, J_1 = 8, J_2 = 2)		6.77 (*dd*, J_1 = 8, J_2 = 2)
H_A-7	2.55*	2.59 (*dd*, J_1 = 13.5, J_2 = 11.5)	3.05–2.21	4.80 (*d*, J = 6.5)	2.72 (*dd*, J_1 = 14, J_2 = 7.5)	4.72 (*d*, J = 7.5)
H_B-7	2.86*	3.03 (*dd*, J_1 = 13.5, J_2 = 3)		—	2.64 (*dd*, J_1 = 14, J_2 = 6.5)	—
H_A-7′	2.95 (*d*, J = 13.5)	2.94 (*br s*)		2.52 (*dd*, J_1 = 13, J_2 = 11)	2.72 (*dd*, J_1 = 14, J_2 = 7.5)	2.95 (*d*, J = 14)
H_B-7′	3.15 (*d*, J = 13.5)			2.96 (*dd*, J_1 = 13, J_2 = 3)	2.64 (*dd*, J_1 = 14, J_2 = 6.5)	3.05 (*d*, J = 14)
H-8	2.55*	1.97 (*m*)		2.30 (*m*)	1.92 (2H, *m*)	2.31 (*ddd*, $J_1 \approx J_2 \approx J_3 \approx$ 6–7)
H-8′	—	—	—	2.69 (*m*)		—
H_A-9	3.97 (*dd*, J_1 = 14, J_2 = 8)	3.61 (*ddd*, J_1 = 11, $J_2 \approx J_3 \approx$ 5)	3.93–3.55	3.90–3.77*	3.69 (*ddd*, J_1 = 11, $J_2 \approx J_3 \approx$ 4)	3.95–3.73 (3H)*
H_B-9	4.02 (*dd*, J_1 = 14, J_2 = 8)	3.76 (*ddd*, J_1 = 11, $J_2 \approx J_3 \approx$ 3–4)			3.54 (*ddd*, J_1 = 11, $J_2 \approx J_3 \approx$ 5)	
H_A-9′	—	3.45 (*dd*, J_1 = 11.5, J_2 = 6)	5.17 and 4.91 (1H, 2 × *d*, J = 4 and 6)	3.67 (*dd*, J_1 = 8.5, J_2 = 6.5)	3.69 (*ddd*, J_1 = 11, $J_2 \approx J_3 \approx$ 4)	
H_B-9′	—	3.51 (*dd*, J_1 = 11.5, J_2 = 4)		3.96 (*dd*, J_1 = 8.5, J_2 = 6.5)	3.54 (*ddd*, J_1 = 11, $J_2 \approx J_3 \approx$ 5)	3.60 (*d*, J = 9)
O–Me	3.79	3.83 (6H, *s*)	3.84 (6H, *br s*)	3.83 (6H, *s*)	3.77 (6H, *s*)	3.83 (6H, *s*)
O–Me′	3.82					
ar-OH	7.44	7.35	7.34 and 7.33	7.37	7.30 (2H, *s*)	7.39
ar-OH′	7.52	7.33	7.43 and 7.34	7.47		7.48
OH-8′	5.16	3.61	3.71 and 3.30	—	—	3.63
OH-9	—	4.42 (*dd*, J_1 = 5, J_2 = 3)	—	—	4.14 (2H, *dd*, $J_1 \approx J_2 \approx$ 4–5)	3.9
OH-9′	—	4.22 (*dd*, J_1 = 6, J_2 = 4)	5.53 and 5.19 (1H, 2 × *d*, J = 4 and 6)	—		—

Coupling constants (J) in Hz.
*Different signals superimposed.

Table 2. ^{13}C NMR data of lignans (in $CDCl_3$)

	10	11	12	14
C-1, C-1′	130.50, 126.27	132.38, 128.20	132.31, 132.14, 128.37, 127.97	132.4
C-2, C-2′	112.97, 111.73	113.28, 111.57	113.24, 113.16, 111.43	111.7
C-3, C-3′	146.87, 146.83	146.68*	146.83, 146.74, 146.70	146.6
C-4, C-4′	145.29, 144.59	144.75, 144.13	145.00, 144.92, 144.25	143.7
C-5, C-5′	114.74, 114.51	114.37*	114.60, 114.45	114.3
C-6, C-6′	123.37, 121.67	123.29, 121.78	123.33, 123.22, 121.43, 121.31	121.5
C-7	31.74	31.89	32.62, 31.94	35.8
C-7′	42.26	40.39	45.32, 38.73	
C-8	43.97	47.60	47.96, 45.61	43.7
C-8′	†	†	82.12, 79.08	
C-9	70.26	61.20	73.10, 71.12	60.5
C-9′	178.67	65.46	103.48, 101.14	
O–Me, O–Me′	56.10, 56.04	56.07	56.08, 56.01	55.7

*Intensity significantly enhanced.
†Hidden under solvent signal.

[mp 120–122°, $[\alpha]_D^{20}$ −118° (EtOH; *c* 0.35)], physicochemical data identical with **15** [20].

Carinol (**11**). C5 was separated over 250 g Sephadex LH 20 with MeOH–$CHCl_3$ (7:3) into five fractions (C5.1–C5.5). The soln of C5.4 in EtOAc was treated with 5% aq. Na_2CO_3, evaporated and rechromatographed over 30 g Si gel ($CHCl_3$–MeOH, 19:1) to give 175 mg of an amorphous powder [$[\alpha]_D^{20}$ −23° (EtOH; *c* 0.4)], physicochemical data identical with **11** [19]. Acetylation (Ac_2O–pyridine) converted the isolated material into a tetra-acetyl derivative, whose spectra were identical with published data for tetra-acetyl-**11** [19].

Methylation of carissanol with MeOH–H$^+$. To a soln of 20 mg **12** in 2 ml MeOH one drop of conc. H_2SO_4 was added and the mixture stirred for 12 hr at room temp., then neutralized with K_2CO_3, filtered and evaporated. The residue was separated by chromatography over Si gel ($CHCl_3$–MeOH, 49:1) into the epimeric methylation products I (amorphous, 6 mg = 29%) and II (amorphous, 10.5 mg = 51%). Epimeric product I: $[\alpha]_D^{20}$ −71.5° (EtOH; *c* 0.2); MS: *m/z* (int. ≥ 5%) 390.1692 $C_{21}H_{26}O_7$ (12, M^+), 206 (5), 193 (30), 180 (5), 175 (9), 164 (5), 163 (15), 161 (6), 151 (7), 150 (15), 143 (6), 138 (41), 137 (100), 133 (6), 131 (8), 124 (9), 123 (7), 122 (11), 115 (5), 94 (9), 77 (8), 65 (5), 55 (14), 51 (5); UV λ_{max}^{EtOH} nm (log ε): 228 (4.01), 280 (3.73); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3550, 2945, 2850, 1612; ^1H NMR ($CDCl_3$): δ6.86 (1H, *d*, *J* = 8 Hz, ar-H), 6.84 (1H, *d*, *J* = 2 Hz, ar-H), 6.81 (1 H, *d*, *J* = 8 Hz, ar-H), 6.74 (1 H, *dd*, J_1 = 8 Hz, J_2 = 2 Hz, ar-H), 6.60 (1H, *dd*, J_1 = 8 Hz, J_2 = 2 Hz, ar-H), 6.54 (1H, *d*, *J* = 2 Hz, ar-H), 5.54 (1H_{ex}, *s*, ar-OH), 5.46 (1H_{ex}, *s*, ar–OH), 4.71 (1H, *s*, $CH\langle^{O}_{O}$), 3.89 (3H, *s*, OCH_3), 3.86 (3H, *s*, OCH_3), 3.82 (1H, *dd*, $J_1 \approx J_2 \approx 8.5$ Hz, OCH_AH_B–CH), 3.72 (1H, $J_1 \approx J_2 \approx 8.5$ Hz, OCH_AH_B–CH), 3.37 (3H, *s*, OCH_3), 3.04 (1H_{ex}, *s*, OH), 2.81 (1H, *d*, *J* = 13.5 Hz, ar-CH_AH_B–C), 2.75 (1H, *d*, *J* = 13.5 Hz, ar-CH_AH_B–C), 2.75 (1H, *dd*, J_1 = 14 Hz, J_2 = 4 Hz, ar-CH_AH_B–CH), 2.45 (1H, *dd*, J_1 = 14 Hz, J_2 = 10.5 Hz, ar-CH_AH_B–CH), 2.24 (1H, *m*). Epimeric product II: $[\alpha]_D^{20}$ +10.5° (EtOH; *c* 1); MS: *m/z* (int. ≥ 5%) 390.1699 $C_{21}H_{26}O_7$ (10, M^+), 206 (6), 194 (6), 193 (33), 180 (5), 175 (9), 164 (5), 163 (8), 161 (7), 151 (8), 150 (16), 143 (7), 139 (6), 138 (42), 137 (100), 133 (7), 131 (5), 124 (10), 123 (6), 122 (11), 94 (9), 77 (8), 65 (5), 55 (15), 51 (5); UV λ_{max}^{EtOH} nm (log ε): 228 (4.05), 279 (3.73); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3540, 2935, 2845, 1608; ^1H NMR ($CDCl_3$): δ6.88 (1H, *d*, *J* = 8 Hz, ar-H), 6.85 (1H, *d*, *J* = 8 Hz, ar-H), 6.83 (1H, *br s*, ar-H), 6.77 (1H, *dd*, J_1 = 8 Hz, J_2 = 2 Hz, ar-H), 6.71 (1H, *dd*, J_1 = 8 Hz, J_2 = 2 Hz, ar-H), 6.69 (1H, *br s*, ar-H), 5.60 (1H_{ex}, *s*, ar-OH), 5.54 (1H_{ex}, *s*, ar-OH), 4.35 (1H, *s*, $CH\langle^{O}_{O}$), 3.97 (1H, *dd*, $J_1 \approx J_2 \approx 8$ Hz, $O\text{–}CH_AH_B\text{–}CH$), 3.89 (6H, *s*, 2 × OCH_3), 3.80 (1H, *dd*, $J_1 \approx J_2 \approx 8$ Hz, $O\text{–}CH_AH_B\text{–}CH$), 3.38 (3H, *s*, OCH_3), 3.05 (1H, *d*, *J* = 14 Hz, ar-CH_AH_B–C), 2.87 (1H, *dd*, J_1 = 12.5 Hz, J_2 = 4 Hz, ar-CH_AH_B–CH), 2.67 (1H, *d*, *J* = 14 Hz, ar-CH_AH_B–C), 2.50–2.74 (2H, *m*), 1.71 (1H_{ex}, *s*, OH).

Conversion of **12** *into* **11**. $LiAlH_4$ (5 mg) was added to a soln of 10 mg **12** in 4 ml Et_2O and stirred for 4 hr at room temp.; excess $LiAlH_4$ was destroyed with EtOAc, then 10 ml 5% aq. HCl was added and the aq. layer extracted × 5 with Et_2O. Combined organic layers were washed, dried and purified by chromatography over 4 g Si gel ($CHCl_3$–MeOH, 19:1) to give 7 mg (= 70%) of an amorphous powder $[\alpha]_D^{20}$ −21° (EtOH; *c* 0.5) identical with **11**.

Preparation of **12** *from* **10**. Compound **10** (25 mg) was dissolved in 5 ml THF (freshly distilled over Na): after addition of 10 mg $LiAlH_4$ the reaction mixture was stirred for 4 hr at room temp. Work-up as described above and chromatography [5 g Si gel, $CHCl_3$–MeOH (49:1)] afforded 8 mg **12** and 5 mg **11**.

Acknowledgements—This work was financially supported by the Deutsche Forschungsgemeinschaft, the Gesellschaft für technische Zusammenarbeit (GTZ) and the Fonds der Chemischen Industrie. Thanks are also due to Mr. A. A. Enti of Forestry Enterprises Ltd., Accra, Ghana, for collection of plant material.

REFERENCES

1. Pakrashi, S. C., Datta, S. and Ghosh-Dastidar, P. P. (1968) *Phytochemistry* **7**, 495.
2. Irvine, F. R. (1961) *Woody Plants of Ghana* p. 617. Oxford University Press, London.
3. Ayensu, E. S. (1978) *Medicinal Plants of West Africa* p. 44. Reference Publications, Algonac.
4. Vohra, M. M. and De, N. N. (1963) *Indian. J. Med. Res.* **51**, 937.
5. Chatterjee, M. L. and Roy, A. R. (1965) *Bull. Calcutta Sch. Trop. Med.* **13**, 14.
6. Jain, M. K. (1965) *Indian J. Appl. Chem.* **28**, 119.
7. Rastogi, R. C., Vohra, M. M., Rastogi, R. P. and Dhar, M. L. (1966) *Indian J. Chem.* **4**, 132.
8. Rastogi, R. C., Rastogi, R. P. and Dhar, M. L. (1967) *Indian J. Chem.* **5**, 215.

9. Singh, B. and Rastogi, R. P. (1972) *Phytochemistry* **11**, 1797.
10. Joglekar, S. N. and Gaitonde, B. B. (1970) *Jpn. J. Pharmacol.* **20**, 367.
11. Plouvier, V. (1965) *C. R. Acad. Sci. Paris* **260**, 1003.
12. Bisset, N. G. (1957) *Ann. Bogor.* **2**, 193.
13. Inouye, H., Okuda, T. and Hayashi, T. (1971) *Tetrahedron Letters* 3615.
14. Shingu, T., Hayashi, T. and Inouye, H. (1971) *Tetrahedron Letters* 3619.
15. Mohr, K., Schindler, O. and Reichstein, T. (1954) *Helv. Chim. Acta* **37**, 462.
16. Joshi, D. V. and Boyce, S. F. (1957) *J. Org. Chem.* **22**, 95.
17. Nishibe, S., Hisada, S. and Inagaki, I. (1971) *Phytochemistry* **10**, 2231.
18. Nishibe, S., Hisada, S. and Inagaki, I. (1973) *Chem. Pharm. Bull.* **21**, 1108.
19. Pal, R., Kulshreshta, D. K. and Rastogi, R. P. (1975) *Phytochemistry* **14**, 2302.
20. Hearon, W. M. and MacGregor, W. S. (1955) *Chem. Rev.* **55**, 957.
21. Briggs, L. H., Cambie, R. C. and Hoare, J. L. (1959) *Tetrahedron Letters* 14.
22. Achenbach, H., Waibel, R., Raffelsberger, B. and Addae-Mensah, I. (1981) *Phytochemistry* **20**, 1591.
23. Stahl, E. (1967) *Dünnschichtchromatographie* 2nd edn, p. 817. Springer, Berlin.
24. Inagaki, I., Hisada, S. and Nishibe, S. (1972) *Chem. Pharm. Bull.* **20**, 2710.
25. Tandon, S. and Rastogi, R. P. (1976) *Phytochemistry* **15**, 1789.
26. Lee, K.-H., Tagahara, K., Suzuki, H., Wu, R. Y., Haruna, M., Hall, I. H., Huang, H.-C., Iida, T., Ito, K. and Lai, J.-S. (1981) *J. Nat. Prod.* **44**, 530.
27. Borris, R. P., Cordell, G. A. and Farnsworth, N. R. (1980) *J. Nat. Prod.* **43**, 641.
28. Kato, A., Hashimoto, Y. and Kidokoro, M. (1979) *J. Nat. Prod.* **42**, 159.
29. Gunasekera, S. P., Cordell, G. A. and Farnsworth, N. R. (1980) *J. Nat. Prod.* **43**, 285.
30. Takehara, T. and Sasaya, T. (1979) *Hokkaido Daigaku Nogakubu Enshurin Kenkyu Hokoku* **36**, 681.