Phytochemistry, 1980, Vol. 19, pp. 2003–2006. © Pergamon Press Ltd. Printed in England. 0031-9422/80/0901-2003 $02.00/0

PTEROCARPANS FROM *SWARTZIA LAEVICARPA**

RAIMUNDO BRAZ FILHO, MIGUEL P. L. DE MORAES and OTTO R. GOTTLIEB†

Instituto de Ciências Exatas, Universidade Federal Rural do Rio de Janeiro, 23460 Seropédica, RJ, Brazil; † Instituto de Química, Universidade de São Paulo, 05508 São Paulo, SP, Brazil

(*Received* 21 *December* 1979)

Key Word Index—*Swartzia laevicarpa*; Leguminosae; pterocarpans; dihydroisocoumarin; isocoumarins; chromone.

Abstract—An ethanol extract of the trunkwood from *Swartzia laevicarpa* (Leguminosae) gave four (6a*R*,11a*R*)-8-hydroxy-3,9-dimethoxypterocarpans differentiated by additional 2-hydroxy, 2-hydroxy-10-methoxy, 4,10-dimethoxy and 2-hydroxy-4,10-dimethoxy substitution; besides two 8-hydroxy-6-methoxy-3-methylisocoumarins differentiated by 5-chloro and 7-chloro substitution; 5-hydroxy-7,8-dimethoxy-2-methylchromone and the known 8-hydroxy-5-methyl-3,4-dihydroxyisocoumarin.

INTRODUCTION

Rationalization of the ethnopharmacological importance of *Swartzia* [2] is not yet possible. In spite of the wide distribution over Africa and chiefly South America, little is known about the chemical composition of the genus. Three of its *ca* 130 species, the African *S. madagascariensis* and *S. leiocalycina* and the South American *S. ulei* Harms were analysed and found to contain pterocarpanoids (Table 1). The present paper reports the occurrence of four additional pterocarpans and of some other constituents in a fourth species, *S. laevicarpa* Amsh. (= *S. benthamiana* Bth.) from a forest near Manaus, Amazonas, which is periodically innundated by the Rio Negro. The species is widely distributed over the basin of the Amazonas river. Its dark heartwood is much appreciated in Manaus, where it is sold under the name 'saboarana' [6].

RESULTS

The four pterocarpans **lj–lm** were recognised as such by the typical NMR signals corresponding to the ABMX-system of four protons [3, 7] and, in the case of **1k**, the three carbons (δ 40.8, C-6a; 66.4, C-6; 78.2, C-11a) of the central oxygen-heterocyclic rings. Assignment of aromatic proton signals by chemical shift and multiplicity is trivial (Table 2), chiefly if the 3,9-dioxygenation pattern, ubiquitous in all 77 previously reported pterocarpanoids, is assumed to exist

Table 1. Substitution of pterocarpanoids from *Swartzia*

	1	2	3	4	6a,11a	8	9	10	Species	Ref.
1a			OH		*R,R*		OMe		*S. madagascariensis*	[3]
1b			OMe		*R,R*		OMe			
1c			OH	OMe	*R,R*		OMe			
1d			OMe	OMe	*R,R*		OMe			
1e			OH		*R,R*	OCH_2O				
1f			OMe		*R,R*	OCH_2O				
1g			OH	OMe	*R,R*	OCH_2O				
1h			OMe	OMe	*R,R*	OCH_2O				
1i		OH	OMe		*R,R*	OCH_2O			*S. leiocalycina*	[4]
1j		OH	OMe		*R,R*	OH	OMe		*S. laevicarpa*	
1k		OH	OMe		*R,R*	OH	OMe	OMe		
1l			OMe	OMe	*R,R*	OH	OMe	OMe		
1m		OH	OMe	OMe	*R,R*	OH	OMe	OMe		
2a			OMe		Δ		OMe		*S. madagascariensis*	[3]
2b			OH	OMe	Δ	OCH_2O			*S. ulei*	[5]
2c	OMe	OH	OMe		Δ	OCH_2O			*S. leiocalycina*	[4]

* Part LVII in the series "The Chemistry of Brazilian Leguminosae". For Part LVI see ref. [1]. Based on the M.S. thesis submitted by M. P. L. de M. to Universidade Federal Rural do Rio de Janeiro, 1979.

Table 2. Comparison of NMR chemical shifts (τ) and multiplicities of aromatic protons for pterocarpans and their acetates (for the doublets $J = 8.5$ Hz)

	1j/acetate	**1k**/acetate	**1l**/acetate	**1m**/acetate
H-1	2.95/2.80 *s*	2.92/2.75 *s*	2.73/2.65 *d*	3.10/2.95 *s*
H-2			3.34/3.25 *d*	
H-4	3.49/3.44 *s*	3.50/3.43 *s*		
H-7	3.15/3.05 *s*	3.40/3.25 *s*	3.40/3.21 *s*	3.40/3.30 *s*
H-10	3.49/3.44 *s*			

also in the present cases. For **1k** hydrogenolysis and MS of the resulting isoflavan **3** revealed the distribution of hydroxy–methoxy groups among the two aromatic rings. The relative location of OH–OMe followed, in all cases, comparative ^{1}H NMR analysis of the spectrum of the compounds and their acetates (Table 2). The assignment of hydroxyls to C-2 and C-3 in **1k** was confirmed by paramagnetic pyridine-induced ^{1}H NMR shifts [8]: $\Delta\delta$ 0.49 (H-1), 0.27 (H-4), 0.46 (H-7); as well as by ^{13}C NMR comparison of the compound and its acetate [9]: paramagnetic shifts of 9.3 (C-1) and 7.8 (C-7). The four pterocarpans **1j**–**1m** are characterized by the same multiple ORD Cotton effects in the 250–350 nm region as the three (−)-pterocarpans from *Dalbegia spruceana* Benth. [10] and must thus possess the same 6a*R*,11a*R*-configuration.

Besides sitosterol and stigmasterol, four additional compounds with molecular formulae $C_{11}H_{12}O_3$ (**4**), $C_{11}H_9ClO_4$ (**5a**, **5b**) and $C_{12}H_{12}O_5$ (**6**) were isolated from the extract. The known dihydroisocoumarin **4** was identified by direct comparison with an authentic sample [11]. Isocoumarin or chromone skeletons were proposed for the remaining three compounds in view of MS, MW, IR and ^{1}H NMR characteristics which included quartets ($J = 0.5$ Hz) for olefinic proton signals. The coupling with methyl protons thus indicated was confirmed by the appearance of C-Me signals as doublets ($J = 0.5$ Hz) and by double resonance experiments. The chemical shifts of the olefinic proton signals, τ 3.34 and 3.36 for **5a** and **5b** vs 3.82 for **6** is diagnostic respectively for isocoumarins (τ 3.3–3.6 [12–15]) vs chromones (τ 3.8–4.1 [16, 17]). The carbonyls of all three compounds are chelated by hydroxyls at the adjacent aromatic positions ($AlCl_3$ shifts of UV maxima). In both isocoumarins these hydroxyls must be *meta*-related with methoxyls, the lone aromatic protons being exposed to the shielding effect of two oxy-substituents (τ 3.47 **5a**, 3.44 **5b**). Finally, the Cl atoms were assigned to C-7 in **5a** and C-5 in **5b** in view of respectively positive and negative Gibbs tests [18]. Acetylation of the chromone results in a 0.22 ppm paramagnetic shift of the ^{1}H NMR singlet at τ 3.62. The lone aromatic proton must thus be either *ortho*- or *para*-related with the hydroxyl, the former alternative (**6**) being more likely in view of a negative Gibbs test [18].

DISCUSSION

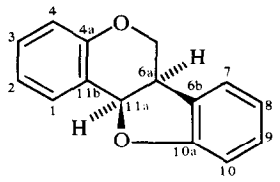
It has been observed [11] that the presence of polyketides, such as isocoumarins and chromones, in the wood of a flowering plant could be due to contamination by fungi during storage prior to extraction. If contamination had occurred again in the present case, the possibly antifungal pterocarpanoids [19] may have been restricted to the resistant heartwood.

EXPERIMENTAL

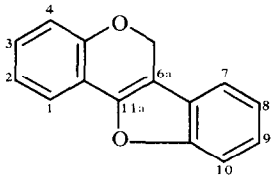
Isolation of the constituents. Percolation of trunkwood (11 kg) with EtOH gave an extract (226 g) which was adsorbed on Si gel. The powder was first washed with petrol and then with C_6H_6. The C_6H_6-eluate (20 g) was chromatographed on Si gel (600 g). Upon elution with $CHCl_3$, 68 successive 250 ml fractions were collected. Evapn of the solvent of fractions 6 (A), 7 (B), 8–10 (C), 19 (D), 20–25 (E), 26–36 (F), 37–39 (G), 60–68 (H) gave the indicated products. A (25 mg), washed with petrol gave **5a** (15 mg). B (15 mg) was washed with C_6H_6–petrol and cryst. from MeOH to **5b** (5 mg). C (40 mg) was rechromatographed on Si gel, $CHCl_3$–C_6H_6, 8:2 eluting a product which, after recryst. in C_6H_6, gave **4** (12 mg). D was cryst. from petrol to sitosterol + stigmasterol (1.2 g). E (1.2 g) was rechromatographed on Si gel, $CHCl_3$ eluting in succession, first a product which, after recryst. from MeOH, gave **6** (18 mg) and next another product which, after recryst. from petrol, gave sitosterol + stigmasterol (450 mg). F was rechromatographed on Si gel, $CHCl_3$ eluting successively 3 products. The first one (50 mg) was cryst. from C_6H_6 into **1l** (20 mg). The residue of the mother liquour gave, upon addition of petrol, **1j** (10 mg). The second one was cryst. from C_6H_6–petrol into **1j** (15 mg). The third one was cryst. from C_6H_6–Me_2CO to **1k** (70 mg). G (100 mg) was cryst. from C_6H_6–Me_2CO to **1k** (20 mg). H (80 mg) was freed from acid impurities by washing of a $CHCl_3$ soln with aq. $NaHCO_3$. The $CHCl_3$ was evapd and the residue cryst. from petrol to **1m** (40 mg).

(6a*R*,11a*R*)-2,8-*Dihydroxy*-3,9-*dimethoxypterocarpan* (**1j**), mp 178–180° (C_6H_6–petrol) [M found: 316.0955; $C_{17}H_{16}O_6$ requires: 316.0947]. ν_{max}^{KBr} cm^{-1}: 3480, 1630, 1600, 1495. λ_{max}^{EtOH} nm: 209, 304 (ε 37 300, 11 050); $\lambda_{max}^{EtOH+NaOH}$ nm: 238, 323 (ε 40 450, 29 400). ^{1}H NMR (100 MHz, $CDCl_3$): τ 6.16, 6.14 (2*s*, 2 OMe), 6.1–6.7 (*m*, H_{ax}-6, H-6a), 5.78 (*dd*, $J = 3.5$, 10.0 Hz, H_{eq}-6), 4.76, 4.74 (2*s*, 2 OH), 4.58 (*d*, $J = 6.0$ Hz, H-11a), 3.49 (*s*, H-4, H-10), 3.15 (*s*, H-7), 2.95 (*s*, H-1). MS (*m/e*): 316 (100%) M$^+$, 315 (9), 301 (50), 177 (9), 164 (28), 149 (19), 121 (6). ORD (*c* 1 mg/25 ml MeOH): $[\phi]_{340}$ + 1220, $[\phi]_{315}^{pk}$ + 11 560, $[\phi]_{308}$ 0, $[\phi]_{300}$ − 24 940, $[\phi]_{230}^{pk}$ − 5470, $[\phi]_{245}^{tr}$ − 32 240, $[\phi]_{23}$ 0. *Acetate*, mp 164–166° (C_6H_6).

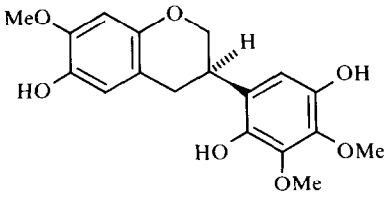
(6a*R*,11a*R*)-2,8-*Dihydroxy*-3,9,10-*trimethoxypterocarpan* (**1k**), mp 126–127° (C_6H_6–Me_2CO) [M found: 346.1060; $C_{18}H_{18}O_7$ requires: 346.1053]. ν_{max}^{KBr} cm^{-1}: 3480, 1620, 1600, 1490. λ_{max}^{EtOH} nm: 207, 300 (ε 28 700, 6900); $\lambda_{max}^{EtOH+NaOH}$ nm: 226, 310 (ε 26 300, 19 050). ^{1}H NMR (60 MHz, $CDCl_3$): τ 6.14, 6.09, 6.00 (3*s*, 3 OMe), 6.0–6.7 (*m*, H_{ax}-6, H-6a), 5.80 (*dd*, $J = 3.5$, 10.0 Hz, H_{eq}-6), 4.60 (*s*, OH), 4.50 (*s*, OH), 4.55 (*d*, $J = 6.0$ Hz, H-11a), 3.50 (*s*, H-4), 3.40 (*s*, H-7), 2.92 (*s*, H-1). ^{13}C NMR (20 MHz, $CDCl_3$): δ 112.1 (*s*, C-11b), 115.3 (*d*, C-1), 140.6 (*s*, C-2), 145.4 (*s*, C-3), 100.1 (*d*, C-4), 148.0 (*s*, C-4a), 66.4 (*t*, C-6), 40.8 (*d*, C-6a), 116.0 (*s*, C-6b), 104.5 (*d*, C-7), 139.0 (*s*, C-8), 143.6 (*s*, C-9), 123.0 (*s*, C-10), 138.0 (*s*, C-10a), 78.2 (*d*, C-11a), 60.3, 61.3 (2*q*, MeO-9, MeO-10), 56.0 (*q*, MeO-3).



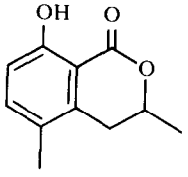
1



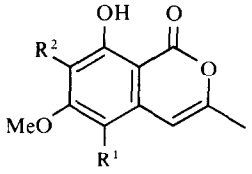
2



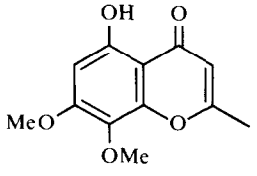
3



4



5a R^1 = Cl, R^2 = H
5b R^1 = H, R^2 = Cl



6

MS (*m/e*): 346 (100 %) M^+, 345 (9), 331 (90), 316 (11), 303 (3), 194 (14), 179 (9), 177 (5), 173 (6), 158 (11), 149 (6). ORD (*c* 1 mg/25 ml MeOH): $[\phi]_{330}$ + 800, $[\phi]^{pk}_{315}$ + 2260, $[\phi]_{306}$ 0, $[\phi]^{tr}_{295}$ − 2930, $[\phi]^{pk}_{280}$ − 1330, $[\phi]^{sh}_{250}$ − 3060, $[\phi]^{tr}_{232}$ − 6790. *Acetate*, mp 115–117° (petrol).

Dihydro derivative. Hydrogenation of **1k** (20 mg) in HOAc (5 ml) over 10 % Pd/C (50 mg) and purification of the product by Si gel chromatography ($CHCl_3$–MeOH 98:2) gave 6,2′,5′-*trihydroxy*-7,3′,4′-*trimethoxyisoflavan*, mp 210–212°. ^{1}H NMR (100 MHz, $CDCl_3$, τ): 7.09 (*d*, *J* = 4.0 Hz, 2H-4), 6.1–6.4 (*m*, H-3), 5.7 (*m*, 2H-2), 6.16, 6.09, 6.06 (3*s*, 3 OMe), 4.8, 4.7, 4.6 (3*s*, 3 OH), 3.60 (*s*, H-8), 3.36 (*s*, H-2), 2.94 (*s*, H-5). MS (*m/e*): 348 (100 %) M^+, 196 (65), 195 (19), 183 (86), 182 (31), 181 (10), 167 (7), 166 (25), 165 (22), 153 (64), 152 (11), 151 (6), 137 (8), 123 (4).

(6aR,11aR)-8-*Hydroxy*-3,4,9,10-*tetramethoxypterocarpan* (**1l**), mp 196–198° (C_6H_6–petrol) [M found: 360.1199; $C_{19}H_{20}O_7$ requires: 360.1209]. ν^{KBr}_{max} cm^{-1}: 3440, 1590, 1500. λ^{EtOH}_{max} nm: 232, 298 (ε 34550, 11 500); $\lambda^{EtOH+NaOH}_{max}$ nm: 274, 315 (ε 18 350, 20 150). ^{1}H NMR (100 MHz, $CDCl_3$): τ 6.14, 6.12, 6.08, 6.01 (4*s*, 4 OMe), 6.1–6.7 (*m*, H_{ax}-6, H-6a), 5.64 (*dd*, *J* = 4.0, 10.0 Hz, H_{eq}-6), 4.55 (*s*, OH), 4.52 (*d*, *J* = 6.0 Hz, H-11a), 3.40 (*s*, H-7), 3.34 (*d*, *J* = 8.5 Hz, H-2), 2.73 (*d*, *J* = 8.5 Hz, H-1). MS (*m/e*): 360 (100 %) M^+, 359 (4), 345 (46), 330 (7), 313 (12), 207 (16), 194 (4), 191 (2), 179 (6), 177 (2), 149 (4). ORD (*c* 2 mg/25 ml MeOH): $[\phi]_{330}$ + 1400, $[\phi]^{pk}_{313}$ + 3500, $[\phi]_{303}$ 0, $[\phi]^{tr}_{283}$ − 10 400, $[\phi]^{pk}_{275}$ − 7600, $[\phi]^{tr}_{245}$ − 30 200 *Acetate*, mp 192–194° (petrol).

(6aR,11aR)-2,8-*Dihydroxy*-3,4,9,10-*tetramethoxypterocarpan* (**1m**), mp 188–190° (C_6H_{14}) [M found: 376.1163; $C_{19}H_{20}O_8$ requires: 376.1158]. ν^{KBr}_{max} cm^{-1}: 3470, 1615, 1600, 1510. λ^{EtOH}_{max} nm: 225, 297 (ε 24 800, 12 800); $\lambda^{EtOH+NaOH}_{max}$ nm: 241, 307 (ε 25 550, 3000). ^{1}H NMR (100 MHz, $CDCl_3$): τ 6.10, 6.08, 6.02, 6.00 (4*s*, 4 OMe), 6.1–6.7 (*m*, H_{ax}-6, H-6a), 5.67 (*dd*, *J* = 3.5, 10.0 Hz, H_{eq}-6), 4.45–4.65 (*m*, 2 OH, H-11a), 3.40 (*s*, H-7), 3.10 (*s*, H-1). MS (*m/e*): 376 (100 %) M^+, 375 (9), 361 (85), 346 (16), 331 (14), 207 (3), 194 (21), 179 (12), 177 (2), 149 (5). ORD (*c* 1 mg/25 ml MeOH): $[\phi]_{330}$ + 3620, $[\phi]^{pk}_{312}$ + 9410, $[\phi]_{307}$ 0, $[\phi]^{tr}_{296}$ − 18 820, $[\phi]^{pk}_{280}$ − 5790, $[\phi]_{238}$ − 37 640. *Acetate*, mp 185–186° (C_6H_{14}).

5-*Chloro*-8-*hydroxy*-6-*methoxy*-3-*methylisocoumarin* (**5a**), mp 155–157° (petrol) [M found: 240.0195; $C_{11}H_9O_4Cl$ requires: 240.0189]. ν^{KBr}_{max} cm^{-1}: 1680, 1640, 1600, 1565, 1480. λ^{EtOH}_{max} nm: 248, 265, 281 infl. (ε 21 150, 5750, 2150); $\lambda^{EtOH+AlCl_3}_{max}$ nm: 240, 266, 274 (ε 16 800, 6500, 6700). ^{1}H NMR (60 MHz, $CDCl_3$): τ 7.70 (*d*, *J* = 0.5 Hz, Me-3), 6.04 (*s*, OMe-6), 3.47 (*s*, H-7), 3.38 (*q*, *J* = 0.5 Hz, H-4), −1.23 (*s*, OH). MS (*m/e*): 242 (40 %) M + 2, 240 (100 %) M^+, 227 (4), 225 (11), 210 (5), 205 (84), 195 (11), 197 (12), 177 (2), 175 (4), 171 (13), 169 (42). *Acetate*, mp 125–127° (C_6H_6). ^{1}H NMR (60 MHz, $CDCl_3$): τ 7.70 (*br.s*, Me-3), 7.58 (*s*, OAc), 5.96 (*s*, OMe), 3.25 (*br.s*, H-1), 3.20 (*s*, H-7).

7-*Chloro*-8-*hydroxy*-6-*methoxy*-3-*methylisocoumarin* (**5b**), mp 163–165° (C_6H_6–MeOH) [M found: 240.0186; $C_{11}H_9O_4Cl$ requires: 240.0189]. ν^{KBr}_{max} cm^{-1}: 1695, 1650, 1600, 1570, 1470. ^{1}H NMR (100 MHz, $CDCl_3$): τ 7.68 (*d*, *J* = 0.5 Hz, Me-3), 6.03 (*s*, OMe-6), 3.44 (*s*, H-5), 3.36 (*q*, *J* = 0.5 Hz, H-4). MS (*m/e*): 242 (35) M + 2, 240 (100 %) M^+, 227 (4), 225 (11), 210 (5), 205 (84), 197 (12), 171 (15), 169 (42).

5-*Hydroxy*-7,8-*dimethoxy*-2-*methylchromone* (**6**), mp 202–203° (MeOH) [M found: 236.0689; $C_{12}H_{12}O_5$ requires: 236.0685]. ν^{KBr}_{max} cm^{-1}: 1675, 1646, 1600, 1580, 1485. λ^{EtOH}_{max} nm: 242, 259, 280 (ε 11 800, 4950, 3750); $\lambda^{EtOH+AlCl_3}_{max}$ nm: 239, 268, 282 (ε 12 900, 5900, 3550). ^{1}H NMR (100 MHz, $CDCl_3$): τ 7.74 (*br.s*, Me-2), 6.09, 6.06 (2*s*, 2 OMe), 3.82 (*br.s*, H-3), 3.62 (*s*, H-6), −1.10 (*s*, OH), MS (*m/e*): 236 (100 %) M^+, 235 (4), 221 (96), 207 (17), 193 (61), 179 (2), 165 (5), 163 (4), 149 (16), 135 (4). *Acetate*, mp 195–197° (MeOH). ^{1}H NMR (100 MHz, $CDCl_3$): τ 7.78 (*br.s*, Me-2), 7.58 (*s*, OAc), 6.12, 6.04 (*s*, 2 OMe), 3.90 (*br.s*, H-3), 3.40 (*s*, H-6).

Acknowledgements—This work was financially supported by Conselho Nacional de Desenvolvimento Científico e Tecnológico. We are grateful to Dr. P. M. Baker, NPPN, Universidade Federal do Rio de Janeiro, for the registry of NMR and MS.

REFERENCES

1. Maranduba, A., Oliveira, A. B. de, Oliveira, G. G. de, Reis, J. E. de P. and Gottlieb, O. R. (1979) *Phytochemistry* **18**, 815.
2. Schultes, R. E. (1979) *J. Ethnopharmacol.* **1**, 79.
3. Harper, S. H., Kemp, A. D. and Underwood, W. G. E. (1969) *J. Chem. Soc. C* 1109.
4. Donnelly, D. M. X. and Fitzgerald, M. A. (1971) *Phytochemistry* **10**, 3147.
5. Formiga, M. D., Gottlieb, O. R., Mendes, P. H., Koketsu, M., Almeida, M. E. L. de, Pereira, M. O. da S., Magalhães, M. T. (1975) *Phytochemistry* **14**, 828.
6. Ducke, A. (1949) *As Leguminosas da Amazônia Brasileira*, 2nd edn, p. 139. Boletim Técnico do Instituto Agronômico do Norte, Belém.
7. Pachler, K. G. and Underwood, W. G. E. (1967) *Tetrahedron* **23**, 1817.
8. Demarco, P. V., Farkas, E., Doddrell, D., Mylari, B. L. and Wenkert, E. (1968) *J. Am. Chem. Soc.* **90**, 5480.
9. Chalmers, A. A., Rall, G. J. H. and Oberholzer, M. E. (1977) *Tetrahedron* **33**, 1735.
10. Cook, J. T., Ollis, W. D., Sutherland, I. O. and Gottlieb, O. R. (1978) *Phytochemistry* **17**, 1419.
11. Alvarenga, M. A. de, Braz Fo., R., Gottlieb, O. R., Dias, J. P. de P., Magalhães, A. F., Magalhães, E. G., Magalhães, G. C. de, Magalhães, M. T., Maia, J. G. S., Marques, R., Marsaioli, A. J., Mesquita, A. A. L., Moraes, A. A. de, Oliveira, A. B. de, Oliveira, G. G. de, Pedreira, G., Pereira, S. A., Pinho, S. L. V., Sant' Ana, A. E. G. and Santos, C. C. (1978) *Phytochemistry* **17**, 511.
12. Aldridge, D. C., Grose, J. F. and Turner, W. B. (1966) *J. Chem. Soc. C* 126.
13. Eaton, M. A. W. and Hutchinson, D. W. (1971) *Tetrahedron Letters* 1337.
14. Guger, H. (1977) *Phytochemistry* **16**, 795.
15. Roberts, J. C. and Woolsen, P. (1970) *J. Chem. Soc. C* 278.
16. Pachler, K. G. R. and Roux, D. G. (1967) *J. Chem. Soc. C* 604.
17. Aberhort, D. J. (1969) *J. Chem. Soc. C* 704.
18. Mesquita, A. A. L., Corrêa, D. de B., Gottlieb, O. R. and Magalhães, M. T. (1968) *Analyt. Chim. Acta* **42**, 311.
19. Harborne, J. B. (1977) *Pure Appl. Chem.* **49**, 1403.