Pergamon 0031-9422(95)0035-6 Phytochemistry, Vol. 40, No. 1, pp. 321-323, 1995
Elsevier Science Ltd
Printed in Great Britain
0031 9422/95 $9.50 + 0.00

α-PYRONES AND THEIR DERIVATIVES FROM TWO *CRYPTOCARYA* SPECIES

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(*Received* 12 *October* 1994)

Key Word Index—*Cryptocarya wyliei*; *C. myrtifolia*; Lauraceae; stem bark; cryptocaryalactone; cyclic derivative of deacetylcryptocaryalactone; cryptofolione oxidation product.

Abstract—From *Cryptocarya myrtifolia*, cryptocaryalactone and its deacetyl derivative have been isolated for only the second time, together with the novel 7-styryl-2,6-dioxabicyclo [3.3.1]nonan-3-one. This cyclic compound could also be obtained by simple transformation of deacetylcryptocaryalactone. *Cryptocarya myrtifolia* also yielded the known cryptofolione and an oxidation product in trace quantities.

INTRODUCTION

Of the indigenous *Cryptocarya* species growing in Southern Africa, three (*C. woodii*, *C. latifolia and C. myrtifolia*) occur as medium to large trees, while *C. wyliei* reaches only shrub height, occurs infrequently and is endemic to Natal Group Sandstones [1]. In preceding papers [2, 3], we have reported on the major chemical constituents of the three larger tree species. These findings and those of the present paper are summarized in Table 1.

DISCUSSION

It is of phytochemical interest to follow some of the trends which become obvious from a study of Table 1. *Cryptocarya woodii* (the commonest species) is not a rich source of α-pyrones. The absence of these compounds may have a bearing on the observation that the Forest Emperor butterfly (*Charaxes xiphares*) selects only this species for breeding purposes (personal communication, A. Balfour-Cunningham).

Cryptocarya latifolia is by far the richest source of α-pyrones and also of the closely related bicyclo compounds, **5** and **6**. We have postulated in a previous paper [3] that they are derived from the open-chain compounds, **2** and **3**. This view is strongly supported by our present finding that deacetylcryptocaryalactone **9** is readily converted into the bicyclo compound **10** by the addition of sodium hydride.

Cryptocarya myrtifolia is unusual in the sense that it contains little other than cryptofolione **4**—up to 0.9% based on the mass of dry, milled bark. The only other compound in *C. myrtifolia* is the cryptofolione derivative **7**. It is present in very low concentration and is reported here for the first time. We are satisfied that it is not an artefact which arises during work-up of the cryptofolione fraction. It occurred in low concentration only but confirmation of structure was unambigous through comparison with authentic material obtained previously [2].

From the bark of *C. wyliei*, one new and three known α-pyrone derivatives were isolated. These are dextrorotatory cryptocaryalactone **8**, racemic deacetylcryptocaryalactone **9**, (+)-goniothalamin **1** and the new racemic bicyclo compound **10**. (+)-Cryptocaryalactone, $[\alpha]_D^{25}$ + 15.5°, was first isolated from *C. bourdilloni* [4] and, subsequently, the (−) isomer, $[\alpha]_D^{27}$ = −20°, was obtained from *C. moschata* seeds [5]. The product isolated by us has $[\alpha]_D^{24}$ = + 56.3°. Surprisingly, the deacetylcryptocaryalactone **9**, reported here was racemic and was also the major component in the bark. Since the spectral data quoted for (+)-cryptocaryalactone by Govindachari [4] is incomplete, and since our compound has a considerably larger rotation, full ^{1}H and ^{13}C information is given in the Experimental. Spencer *et al.* [5, 6] provide very little information about their (−)-deacetylcryptocaryalactone, so that again a full spectral analysis is given.

The new bicyclo compound **10** is an analogue of the bicyclic α-pyrone derivatives found by us in *C. latifolia* [2]. By applying standard COSY and HETCOR analysis and by comparison with the ^{1}H and ^{13}C NMR information available for **5** and **6**, its structure was readily determined.

Scrutiny of the data in Table 1 emphasizes the fact that *C. wyliei* is chemically quite distinct from the other three

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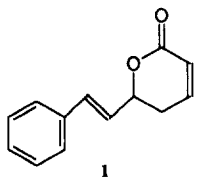

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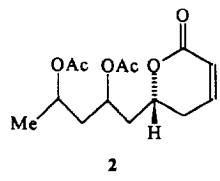

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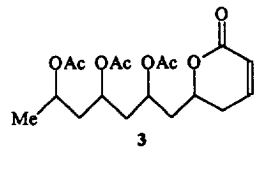

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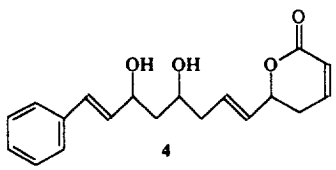

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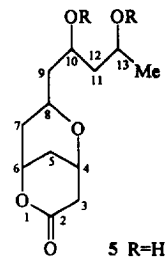

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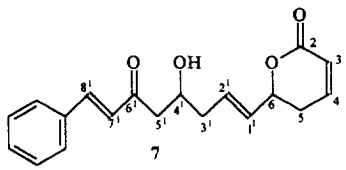

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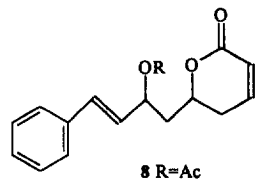

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9 R=H

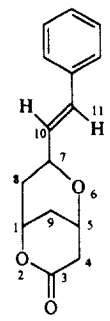

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Table 1. α-Pyrones and related compounds in *Cryptocarya* species

Compoound	*C. woodii*	*C. latifolia*	*C. myrtifolia*	*C. wyliei*
Goniothalamin (1)	*	√	—	√
α-Pyrone (2)	—	√	—	—
α-Pyrone (3)	trace	High	trace	—
Cryptofolione (4)	trace	√	Very high	trace
Bicyclo compound (5)	—	low	Nil	trace
Bicyclo compound (6)	—	low	Nil	—
Cryptofolione ketone (7)	—	—	trace	—
Cryptocaryalactone (8)	—	—	—	√
Deacetyl cryptocaryalactone (9)	—	—	—	√
Bicyclo compound (10)	—	—	—	√

*Where √ means present.

Cryptocarya species. The α-pyrones it contains belong exclusively to the goniothalamin 1/cryptofolione 4 series in the sense that there is a styryl residue attached to the side-chain terminus.

EXPERIMENTAL

General. NMR: ^{1}H(200 MHz) and ^{13}C (50 MHz); EIMS: 70 eV; CC: silica gel 60 (Macherey Nagel); Chromatotron: silica gel 60 F_{254}.

Plant material. Cryptocarya wyliei Stapf stem bark was collected in May 1994 from trees growing in the Umtamvuma Nature Reserve (South Coast, Kwazulu-Natal). A voucher specimen (identified by R.W-S) is lodged in the Killick Herbarium (CPF) no. 6084.

Isolation. Milled bark (686 g) was sucessively extracted at 35°, with petrol (60–80°), CH_2Cl_2 EtOAc and EtOH. The α-pyrone derivatives were all located in the petrol (2 g), CH_2Cl_2 (6.2 g) and EtOAc (4.3 g) frs. Individual separation on CC and by Chromatotron (using CH_2Cl_2–EtOAc mixts) afforded four compounds.

(+)-*Goniothalamin* (**1**). (395 mg). $[\alpha]_D^{24}$ +183.9°, lit. [7] 178.5°. Otherwise identical spectral properties to those reported in the lit.

(+)-*Cryptocaryalactone* (**8**). Oil, (34.7 mg). $[\alpha]_D^{24}$ + 56.3 ($CHCl_3$; *c* 0.003). IR ν_{max} cm^{-1}: 1730 (br), 1601, 1494, 1380, 1230, 1078, 1037, 968. ^1H NMR ($CDCl_3$, 200 MHz): δ2.03 (1H, *m*, H-1^{1}a), 2.39 (1H, *m*, H-1^{1}b), 2.43 (2H, *m*, H-5), 4.52 (1H, *m*, H-6), 5.67 (1H, *m*, *J* = 5.7 Hz, H-2^1), 6.03 (1H, *m*, H-3), 6.11 (1H, *dd*, *J* = 15.9, 7.6 Hz, H-3^1), 6.70 (1H, *dd*, *J* = 16.0, 0.6 Hz, H-4^1), 6.88 (1H, *m*, H-4), 7.25–7.45 (5H, *m*, Ar-H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ21.3 (OAc), 29.4 (C-5), 39.7 (C-1^1), 71.2 (C-2^1), 74.7 (C-6), 121.5 (C-3), 126.0 (C-3^1), 126.7, 128.3, 128.6, 135.8 (Ar-C), 133.9 (C-4^1), 144.6 (C-4), 163.8 (pyrone C=O), 170.1 (OCOMe). MS *m/z* (rel. int.): 286 (C-1^1) (18), 244 (8), 226 (32), 159 (90), 131 (100), 104 (60), 97 (75), 43 (94). HR-MS: $[M]^+$ 286.1227; calcd. for $C_{17}H_{18}O_4$ 286.1205.

(+)-*Deacetylcryptocaryalactone* (**9**). Crystals (210 mg). mp 65–68°. $[\alpha]_D^{24}$ − 0.0°. IR ν_{max} cm^{-1}: 3350 (OH), 1708 (C=O), 1394, 1269, 1010, 966, 756. ^1H NMR ($CDCl_3$, 200 MHz): δ1.90 (1H, *m*, H-1^{1}a), 2.20 (1H, *m*, H-1^{1}b), 2.41 (2H, *m*, H-5), 4.59 (2H, *m*, H-6 and H-2^1), 4.78 (1H, *s*, OH), 5.98 (1H, *m*, H-3), 6.18 (1H, *dd*, *J* = 15.9, 7.0 Hz, H-3^1), 6.63 (1H, *dd*, *J* = 15.9, 7.0 Hz, H-3^1), 6.63 (1H, *dd*, *J* = 15.9, H-4^1), 6.85 (1H, *m*, H-4), 7.20–7.45 (5H, *m*, Ar-H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ29.4 (C-5), 41.9 (C-1^1), 69.6 (C-2^1), 75.9 (C-6), 121.1 (C-3), 126.5, 127.9, 128.6 and 136.2 (Ar-C), 130.9 (C-3^1), 131.3 (C-4^1), 145.4 (C-4), 164.3 (pyrone C=O). MS *m/z* (rel. int.): 244 $[M]^+$ (12), 158 (25), 133 (27), 104 (100) $[C_6H_5CH = CH_2^+)]$, 97 (28), 94 (25), 91 (20), 77 (12). HR-MS: $[M]^+$ 244.1093; calcd. for $C_{15}H_{16}O_3$ 244.1099.

7-Styryl-2,6-dioxabicyclo[3,3,1] *nonan-3-one* (**10**). Crystals (18.6 mg). Racemic. IR ν_{max} cm^{-1}: 1730 (C=O), 1608, 1341, 1218, 1080, 758. ^1H NMR ($CDCl_3$, 200 MHz): δ1.77 (1H, *ddd*, *J* = 14.0, 2.2 Hz, H-8a), 2.14 (1H, *m*, H-8b), 1.99 (2H, *m*, H-9), 2.83 (1H, *dd*, *J* = 19.3, 5.0 Hz, H-4a), 2.98 (1H, *m*, H-4b), 4.45 (2H, *m*, H-5, H-7), 4.95 (1H, *m*, H-1), 6.14 (1H, *dd*, *J* = 16.0, 6.1 Hz, H-10), 6.64 (1H, *dd*, *J* = 16.0, 1.1 Hz, H-11), 7.23–7.41 (5H, *m*, Ar-H). ^{13}C NMR ($CDCl_3$, 50 MHz,): 29.5 (C-9), 36.5 (C-4), 37.2 (C-8), 66.1 and 66.8 (C-5, C-7 or reverse), 72.8 (C-1), 127.9 (C-10), 126.5, 128.1, 128.6, 136.2 (Ar-C), 131.6 (C-11), 169.6 (pyrone C=O). MS *m/z* (rel. int.): 244 (8), 184 (6), 158 (6), 131 (25), 115 (12), 104 (100), 91 (15), 77 (11), 70 (26). HR-MS: $[M]^+$ 244.1086; calcd. for $C_{15}H_{16}O_3$ 244.1099.

Cyclization of deacetylcryptocaryalactone (**9**) to (**10**). Deacetylcryptocaryalactone (200 mg) in CH_2Cl_2 (5 ml) was treated with excess NaH. After 5 min, the reaction was quenched (EtOAc) and the pp. filtered off. On standing, fine needles formed (160 mg) which were purified on the chromatotron (CH_2Cl_2) and finally recrystallized from CH_2Cl_2–hexane (80 mg), mp 69°. The compound was identical in all respects to the bicyclononane (**10**) found occuring naturally in the bark.

Plant material. Cryptocarya myrtifolia Stapf stem bark (1.54 kg) was collected in May 1994 from specimens growing in the Karkloof Nature Reserve (District Pietermaritzburg), Kwazulu-Natal. A voucher specimen No.6083 is lodged in the KillickHerbarium (CPF).

Extraction, first with petrol then with CH_2Cl_2 and EtOAc, yielded 11.51 g and 8.0 g of oil, respectively. Using the procedures described earlier [2], a total amount of 14 g of cryptofolione was isolated. The other constituent described (below) was present in much lower concentration.

The two extracts above were each separately chromatographed on silica gel with hexane–EtOAc (49:0.1) and then furhter purified on the Chromatotron with Et_2O–EtOAc (7:3) to give 120 mg of purified product. Examination of the ^1H and ^{13}C NMR of the pure compound indicated that it was identical to the product obtained from oxidation of cryptofolione which we reported earlier [2]. The compound is, thus, 6-(4^1-hydroxy-6^{1}oxo-8^1-phenyloct-1,1^7-dienyl)-5,6-dihydro-2H-pyran-2-one (**7**). This compound is easily distinguished from cryptofolione by the presence of the two clear doublet signals (*J* = 16.3 Hz) in the ^1H NMR due to the presence of the styryl moiety in the down-field region.

Acknowledgements—The authors thank the Foundation for Research Development (FRD) and the University Research Fund for financial assistance.

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