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α-PYRONE FROM *CRYPTOCARYA LATIFOLIA*—A STRUCTURAL ISOMER OF UMURAVUMBOLIDE

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Key Word Index—*Cryptocarya latifolia*; Lauraceae; bark; 6-substituted 5,6-dihydro-α-pyrone; umuravumbolide.

Abstract—A new 6-substituted 5,6-dihydro-α-pyrone with a terminal ethyl group has been obtained as a minor component from *Cryptocarya latifolia*. It is a structural isomer of umuravumbolide, but has a *trans* exocyclic double bond.

INTRODUCTION

In an earlier communication we have reported on 6-substituted 5,6-dihydro-α-pyrones (and cyclic derivatives of these), which occur as major constituents in *Cryptocarya latifolia* Sond [1]. A common feature of these compounds was the saturated side chain attached to C-6, being heptyl in **1** and pentyl in **2**.

The α-pyrone described here (**3**) has one double bond in the side chain and is in fact a structural isomer of umuravumbolide (**4**), isolated in 1979 by Van Puyevelde *et al.* [2] from Rwandan *Tetradenia* (formerly *Iboza*) *riparia*. Recently, this somewhat ellusive α-pyrone has been re-isolated from a southern African *Tetradenia* species by Davies-Coleman and Rivett [3]. These authors were able to show conclusively, using Mosher's method, that **4** possesses the (3′*S*)-configuration.

RESULTS AND DISCUSSION

Re-examination of the bark extracts from *C. latifolia*, which are dominated by the high concentration of **1** (0.23%), indicated trace quantities of a new compound in 0.003% overall yield based on milled bark. Inspection of its ^{1}H NMR spectrum (200 MHz) left no doubt that the α-pyrone nucleus was present as shown by the characteristic resonances at δ4.5 (H-6), 6.02 (H-3, *ddd*) and 9 (H-4). Downfield peaks at δ5.2–5.6 from resonances of protons obviously coupled with one another, indicated unsaturation in the side chain. The coupling constant between the two protons on the exocyclic double bond ($J_{4',5'}$) is 15.3 Hz, and can be measured unambiguously despite the complexity (*dtt*) of the resonance signals. This stands in contrast to the finding of Davies-Coleman and Rivett [3] in **4**, which possesses a *cis* exocyclic double bond (J = 11.0 Hz). These assignments of configuration can be made with confidence following the work of Valverde *et al.* [4].

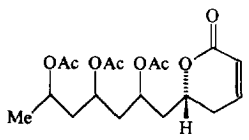
Out of interest we have re-examined our other compounds from Lauraceae bearing exocyclic double bonds, i.e. cryptofolione [5], cryptocaryalactone and deacetyl cryptocarylalactone [6] and 7-styryl-2,6-dioxabicyclo [3.3.1]nonan-3-one [6]. In all these instances a *trans-configuration pertains* (J = 15.5–15.9 Hz). Also, all these compounds show an IR absorbance at 965–975 cm^{-1}, in accordance with the observed stereochemistry [7].

Comparison of the ^{1}H, ^{13}C, COSY and HETCOR spectra of **3** with those recorded for cryptocaryalactone (**5**) [5] simplified the task of assigning the overall structure as (2′-acetoxy)-6-hept-4-enyl-5,6-dihydro-2-H-pyran-2-one (**3**). High resolution EI mass spectrometry confirmed the presence of a molecular ion of composition $C_{14}H_{20}O_4$.

EXPERIMENTAL

Isolation of (2′-acetoxy)-6-hept-4-enyl-5,6-dihydro-2-H-pyran-2-one (**3**). Bark from mature trees of *C. latifolia* growing in the Karkloof area of Kwazulu-Natal was finely ground and extracted. A voucher specimen (No. 6095) has been deposited in the Killick Herbarium (CPF), Natal Parks Board, Queen Elizabeth Park, S. Africa.

Extraction of bark (4.4 kg) with CH_2Cl_2 afforded an oil (81 g). Purification by flash chromatography using hexane–Et_2O (3:2) as eluent gave an oil (14 mg), $[\alpha]_D^{28}$ + 97.8° ($CHCl_3$; *c* 1.4). ν_{max}^{NaCl} cm^{-1}. 3350, 1720, 1480, 1350, 1040; 971. ^{1}H NMR (200 MHz, $CDCl_3$): δ0.96 (3H, *t*, J = 7.5 Hz, H-7′), 2.04 (2H, *m*, H-6′), 2.04 (1H, *m*, H_a), 2.22 (1H, *m*, H_b), 2.30 (1H, *m*, H-5$_a$), 2.47 (1H, *m*, H5$_b$),



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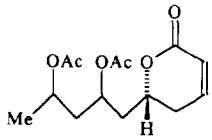

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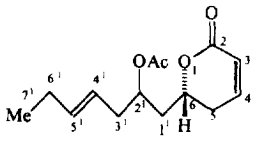

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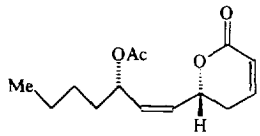

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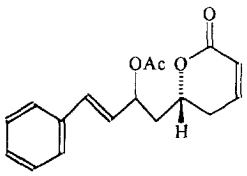

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4.49 (1H, *m*, $J = 8.8$ Hz, H-6), 5.04 (1H, *m*, H-2′), 5.31 (1H, *dtt*, $J = 15.27$, 6.98, 1.46 Hz, H-4′), 5.56 (1H, *dtt*, $J = 15.29$, 6.23, 1.02 Hz, H-5′), 6.02 (1H, *ddd*, $J = 9.8$, H-3), 6.87 (1H, *m*, $J = 9.8$ Hz, H-4); ^{13}C NMR (50 MHz, $CDCl_3$): δ13.7 (C-7′), 21.1 (acetyl), 25.6 (C-6′), 29.1 (C-5), 37.8 (C-3′), 38.7 (C-1′), 70.0 (C-2′), 75.2 (C-6), 121.4 (C-3), 122.9 (C-4′), 136.4 (C-5′), 144.7 (C-4), 164.0 (C-2), 170.8 (acetyl); HREIMS: observed $m/z = 252.1329$, $C_{14}H_{20}O_4$ requires 252.1361.

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