terised by the following ^{1}H NMR bands, δ_H 7 98*s*, 7 38*s*, 6 72*s*, 4 64*s*, 3 64*m*, 3 52*s* and methyl groups

One of us (S M A) is grateful to the C S I R for a maintenance grant while carrying out this work

REFERENCES

1 Adesida, G A and Taylor, D A H , (1967) *Phytochemistry* **6**, 1429
2 Okorie, D A and Taylor, D A H (1977) *Phytochemistry* **16**, 2029
3 Arndt, R R and Baarschers, W H (1972) *Tetrahedron* **28**, 2333
4 Bevan, C W L , Ekong D E U , Halsall, T G and Toft P (1967) *J Chem Soc (C)* 820
5 Connolly, J D , Labbe, C and Rycroft, D S (1978) *J Chem Soc Perkin Trans 1*, 285
6 Rao, M M , Gupta, A S , Singh, P P and Krishna E M (1979) *Indian J Chem* 17B, 158
7 Ragettli, T and Tamm, Ch (1978) *Helv Chem Acta* **61**, 1814
8 Taylor, D A H (1979) *Phytochemistry* **18**, 1574
9 Srivastava, S D (1986) *J Nat Prod* **49**, 56

Phytochemistry, Vol 27 No 4, pp 1220 1221, 1988
Printed in Great Britain

0031 9422/88 $3 00 + 0 00

PROTOLIMONOIDS FROM *TURRAEA NILOTICA*

DULCIE A MULHOLLAND and DAVID A H TAYLOR

Department of Chemistry, University of Natal, Durban, R S.A

(*Revised received* 14 *August* 1987)

Key Word Index—*Turraea nilotica*, Meliaceae, protolimonoid

Abstract—*Turraea nilotica* has been found to yield a new protolimonoid, 24,25 epoxy-23-hydroxy-7-tirucallen-3-one, which we name niloticin, together with two closely related compounds No limonoids were found.

INTRODUCTION

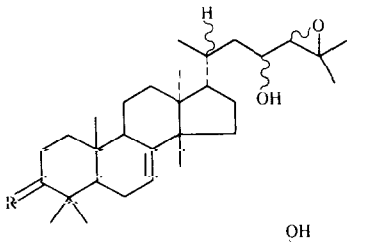
Turraea (Meliaceae, tribe Turraeeae) is a rather variable genus, containing at the most recent delimitation [1] some 60–70 species of shrubs and small trees in the Indian Ocean area We have recently shown [2] that *T obtusifolia* (section Euturraea) contains the complex limonoid prieurianin, while *T floribunda* (section Rutaea) contains simpler limonoids of the havanensin type It would be interesting to know whether this difference is taxonomically significant or not; unfortunately although *Turraea* species are widespread they are nowhere common, or at least are inconspicuous, and correspondingly difficult to obtain We now report examination of *T nilotica* Kotschy et Peyr (also section Rutaea) collected and supplied by the scientific staff of the Kruger Park

RESULTS AND DISCUSSION

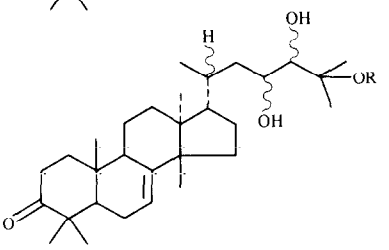
Extraction of pulverized stem of *T nilotica* (wood and bark) with petrol gave an extract which yielded one major crystalline protolimonoid niloticin, and two minor ones, one crystalline, one amorphous; but no limonoids The major product gave spectra suggesting that it was a stereoisomer of 24,25-epoxy-23-hydroxy-7-tirucallene-3-one **1** (=21 deoxy-melianone) The spectra were in general similar to those of melianone [3], showing the epoxide carbons δ_C 68 4*d* and 59 8*s* and the characteristic H-24 epoxide doublet (δ_H 2.67, J = 8 1 Hz). However the hemiacetal signals associated with C-21 in melianone were missing, and instead there was a secondary methyl resonance (δ_H 0 96, J = 6 Hz)

The presence of the epoxide was chemically confirmed by methanolysis, giving a 24-hydroxy-25-methoxy derivative **2**, the position of the hydroxy-epoxide was chemically confirmed by periodate oxidation, which gave a tetra-noraldehyde **3** This leaves the stereochemistry undetermined. The most commonly occurring arrangement is that of melianone, with the tirucallol 20αH and the 23*R*-24*R* configuration However, both 24*R* and 24*S* configurations have been identified [4, 5], we have no evidence to show which is present in niloticin

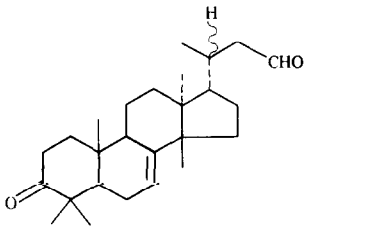
The second product, also crystalline but isolated in small yield, was a dihydroniloticin The spectra were similar to those of niloticin, but instead of a ketonic carbonyl, showed an extra secondary alcohol The ^{1}H NMR spectrum (δ 3 21, $W_{1/2}$ = 14 4 Hz) showed dihydroniloticin to be an equatorial alcohol; it is therefore the 3β alcohol **4** corresponding to the ketone niloticin It is interesting that protolimonoids, as for example turraean-



1 R = O
4 R = H 3βOH



2 R = Me
5 R = H



3

thin, often have the 3β oxygenated configuration, whereas so far limonoid 3- alcohols always have the α-configuration. It is possible this may have biosynthetic significance.

The third compound, which remained amorphous, contained the elements of a molecule of water in excess of nilotic in; and had lost the epoxide. Otherwise the ^{13}C NMR spectrum was identical This compound is therefore the triol **5** obtained by hydrolysis of the oxide in nilotic in, (δ_C 74.9*s*, 74.2*d* instead of 59 8*s*, 68 4*d*)

EXPERIMENTAL

Extraction Turraea nilotica wood and bark (3 kg, supplied by the scientific staff of the Kruger Park) was pulverized and percolated with refluxing hexane The extract was partitioned with 95% MeOH, the MeOH diluted to 50% and extracted with CH_2Cl_2 and the latter evaporated, yielding a gum (5 4 g) Chromatography gave *nilotic in* **1** as a crystalline solid (2 7 g), m.p. 149° $[\alpha]_D^{23}$ −70 9° [Found, *m/z* 456, $C_{30}H_{48}O_3$ requires 456 δC 216 2*s*, 145 6*s*, 117 8*d*, 69 0*d*, 68 4*d*, 59 8*s*, 53 1*d*, 52 2*d*, 51 1*s*, 48 4*d*, 47 7*s*, 43 5*s*, 40 7*t*, 38 4*t*, 34 9*s*, 34 7*t*, 33 9*t*, 33 5*t*, 33 5*d*, 28 5*t*, 27 2*q*, 24 7*q*, 24 5*q*, 24 2*t*, 21 6*q*, 21 4*q*, 19 8*q*, 19 6*q*, 18 1*t*, 12 6*q* δ_H 5 32 (*m* H-7), 3 57 (*m* H-23), 2 67 (*d*, *J* = 8 1 Hz, H-24), 1 32, 1 32, 1.12, 1 05, 1 02, 1 00, 0 96 (*d*, *J* = 6 Hz) 0 81 (Me groups)]

Dihydronilotic in **4** was also crystalline, mp 175°, obtained in small amount [Found, *m/z* 458, $C_{30}H_{50}O_3$ requires 458 δ_C 145 6*s*, 118 1*d*, 79 2*d*, 69 3*d*, 68 6*d*, 59 8*s*, 53 3*d*, 51 2*s*, 50 7*s*, 49 0*d*, 43 6*s*, 40 8*t*, 39 0*t*, 37 3*s*, 36 1*t*, 35 0*d*, 34 0*t*, 33 9*t*, 33 6*d*, 28 8*t*, 27 7*q*, 27 2*q*, 24 9*q*, 24 0*t*, 21 7*q*, 20 0*q*, 19 8*q*, 18 1*t*, 14 7*5q*, 13 1*q* δ_H 5.26 (*m* H-7), 3.51 (*m* H-23), 3 21 (*m* $W_{1/2}$ 14.4 Hz, H-3), 2 62 (*d*, *J* = 8 1 Hz, H-24), 1 30, 1 30, 0 95, 0 95, 0 91 (*d*, *J* = 6), 0 84, 0 79, 0 72]

The triol **5** remained amorphous. [Found *m/z* 474; $C_{30}H_{50}O_4$ requires 474. δ_C 217 0*s*, 145 7*s*, 117 8*d*, 74 9*s*, 74 2*d*, 69 6*d*, 53 7*d*, 52 2*d*, 51 0*s*, 48 3*d*, 47 8*s*, 43 4*s*, 40 3*t*, 38 4*t*, 34 9*t*, 34 8*s*, 33 9*t*, 33 7*t*, 33 6*d*, 28 3*t*, 27 2*q*, 27 2*q*, 26 1*q*, 24 7*q*, 24 4*t*, 24 2*q*, 21 9*q*, 21 5*q*, 18 8*t*, 12 7*q* δ_H 5 18 (*m* H-7), 4 0 (*m* H-23), (3 35*d*, *J* = 8 Hz, H-24), 1, 25, 1 25, 1.20, 1 12, 1.05, 0 96 (*d*, *J* = 6 Hz), 0 95, 0 75]

Methanolysis of nilotic in Nilotic in **1** (223 mg) was refluxed with sulphuric acid (50 ml, 1 N in 50% MeOH) for 0 5 hr The product **2** isolated with ether, was amorphous Acetylation gave a crystalline diacetate (149 mg) mp 174–175°. [Found *m/z* 572, $C_{35}H_{50}O_6$ requires 572 δ_C 216 1*s*, 170 1*s*, 168 4*s*, 145 6*s*, 117 3*d*, 76 1*s*, 75 0*d*, 69 6*d*, 53 5*d*, 52 1*q*, 51.0*s*, 49.4*d*, 48 3*d*, 47.6*s*, 43 4*s*, 38 2*d*, 38.0*t*, 34 8*s*, 34.7*t*, 33 8*t*, 33 7*t*, 32 9*t*, 27 6*t*, 27 2*q*, 24 4*q*, 24 2*t*, 22 5*q*, 21 7*t*, 21 4*q*, 21 1*q*, 20 9*q*, 20 6*q*, 18 2*q*, 18 2*q*, 12 6*q* δ_H 5 46 (*m* H-23), 5.35 (*m* H-7), 5 0 (*d*, *J* = 2 Hz, H-21), 3 20 (OMe), 2 16, 2 05 (OAc), 1 17, 1.16, 1.11, 1 05, 0 99, 0 98, 0 96 (*d*, *J* = 6 Hz) 0.81 (Me)

Periodate oxidation of nilotic in Sodium periodate (400 mg) in water (1 5 ml) and perchloric acid (70%, 1 drop was added to nilotic in **1** (211 mg) in dioxan (20 ml), and left 1 hr The aldehyde **3** (129 mg), isolated with ether did not crystallize [Found *m/z* 384, $C_{26}H_{40}O_2$ required 384 δ_C 216 4*s*, 203 0*d*, 145 6*s*, 118 0*d*, 52 7*d*, 52 3*d*, 51 2*s*, 50.8*d*, 48 4*d*, 47 7*s*, 43 6*s*, 38 4*t*, 35 0*s*, 34 8*t*, 33 9*t*, 33 5*t*, 31 9*t*, 28 3*t*, 27 3*q*, 24 5*q*, 24 3*t*, 21 8*q*, 21 5*q*, 19 6*q*, 18 15*t*, 12 7*q* δ_H 9 68 (*m* H-23), 5 24 (*m* H-7) methyl region unresolved]

Acknowledgement—This work was supported by a grant from the Research Grants Division of the C S I R

REFERENCES

1 Pennington, T D and Styles, B T (1975) *Blumea* **22**, 457
2 Akinniyi, J A, Connolly, J D, Mulholland, D. A, Rycroft, D S and Taylor, D A H (1986) *Phytochemistry* **25**, 2187
3 Lavie, P, Jain, M K and Kirson, I (1967) *J Chem. Soc* (C) 1347
4 Connolly, J D, Labbé, C, Rycroft, D S and Taylor, D A H (1979) *J Chem. Soc, Perkin. Trans. I*, 2954
5 Chan, W R, Taylor, D R and Yee, T (1971) *J Chem. Soc* (C) 2662