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3-FARNESYLINDOLE FROM *UVARIA PANDENSIS* VERDC.

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Key Word Index—*Uvaria pandensis*; Annonaceae; indolosesquiterpene; 3-farnesylindole.

Abstract—The new indolosesquiterpene, 3-farnesylindole, has been isolated from *Uvaria pandensis*., in addition to farnesol and α-tocopherol.

INTRODUCTION

3,6-Bis(γ,γ-dimethylallyl)indole, an indole substituted only by two unlinked isoprenoid units, was isolated from a West African *Uvaria* species, *Uvaria elliotiana* [1], and also from *Hexalobus crispiflorus* (Annonaceae) [2]. We hereby report on the isolation of a similar indolosesquiterpene, 3-farnesylindole, from *Uvaria pandensis* Verdc.* which is used locally in the vicinity of Dar es Salaam to treat fevers and stomach disorders.

RESULTS AND DISCUSSION

From the petrol extract of the leaves of *Uvaria pandensis* three terpenoids were isolated by silica gel chromatography. These included a new indolosesquiterpene, 3-farnesylindole (**1**), farnesol, and α-tocopherol. Compound **1** is an oil, $C_{23}H_{31}N$ ($[M]^+$ at m/z 321). The presence of an indole moiety in **1** was indicated by the UV absorption maxima at 280 and 290 nm, as well as the IR absorption bands at 3490 cm^{-1} (=NH group) and at 735 cm^{-1} (disubstituted benzene). The IR spectrum also showed the presence of the isolated double bonds in the farnesyl moiety (1620 and 1665 cm^{-1}). The presence of an indole group in **1** was also indicated by a ^1H NMR signal at δ7.95 (1H, =NH), three aromatic proton resonances in the region δ7.0–7.5 (complex *m*, 3H; H-5, H-6 and H-7) and aromatic proton signals at δ7.6–7.7 (*m*, 1H, H-4) and δ6.85 (*br s*, 1H, H-2). The position of the farnesyl substituent in the indole ring system was based upon comparison of the ^1H NMR spectrum of **1** with other monosubstituted indoles [3–6].

The high field resonances at δ1.60 (*s*, 6H), 1.67 (*s*, 3H), 1.75 (*s*, 3H) and 1.9–2.2 (*m*, 8H) as well as the signals at δ3.45 (*t*, $J = 7$ Hz, 1H) showed that the substituent at indole C-3 is a farnesyl group [7]. The mass spectral fragment ions at m/z 184 $[M - C_{10}H_{17}]^+$ and 130 (base peak), ($[M - C_{14}H_{23}]^+$) are in agreement with the identity of a farnesyl group as the substituent. The 3′-Me, 7′-Me, C-4′ and C-8′ chemical shifts in the ^{13}C NMR spectrum of **1** are particularly indicative for the stereochemistry of the double bonds of the farnesyl group in **1**. The chemical shifts of both the 3′-Me and 7′-Me carbons in a (2*E*, 6*E*)-farnesyl moiety can be expected to approximate δ16, as observed for (2*E*, 6*E*)-farnesol [8]. This is very close to the values for 3′-Me and 7′-Me in the ^{13}C NMR spectrum of **1** (δ16.5 and 14.9, respectively, see Table 1). Similarly the C-4′ and C-8′ chemical shifts for the farnesyl groups in **1** are both at δ38.7. This value compares well with C-4′ and C-8′ chemical shifts in the spectrum of (2*E*, 6*E*)-farnesol (δ39.7 and 39.6, respectively) [8]. The absence of a signal in the region δ30–33 in the ^{13}C NMR spectrum of **1** rules out the other possible stereochemical configurations (2*E*, 6*Z*, 2*Z*, 6*Z* or 2*Z*, 6*E*) for the farnesyl group in **1** [8].

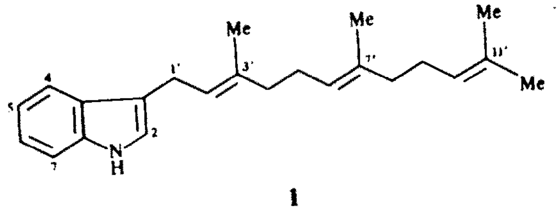
The tentative assignment of the chemical shifts in Table 1 compare well with ^{13}C NMR data for farnesol [8] and 3-methylindole [9]. The chemical shifts for the farnesyl moiety in **1** were as expected slightly shifted upfield, when compared with farnesol [8].

The identity of α-tocopherol and farnesol was on the basis of the comparison of the ^1H NMR and mass spectral data with literature values.

EXPERIMENTAL

Isolation of 3-farnesylindole (**1**). Air-dried ground leaves (800 g) were extracted for 48 hr with petrol (bp 40–60°). CC of the crude extract on silica gel (CH_2Cl_2–petrol, 1:4) gave crude **1** which was purified by repeated prep. TLC (silica gel F254, 2 mm thickness, CH_2Cl_2–petrol, 1:4). Further chromatography of the crude extract gave a fraction containing a mixture of farnesol, α-tocopherol and an unidentified sesquiterpene, which was also separated by prep. TLC.

3-*Farnesylindole* (**1**). Oil (300 mg, 0.04 %); UV λ_{max}^{hex} nm: 280 and 290. IR, ν_{max} cm^{-1}: 3490, 3080, 3060, 1665, 1620, 1455, and 735;



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* The name *Uvaria pandensis* Verdc. has been proposed by Dr B. Verdcourt of the Royal Botanic Gardens in England. A reference specimen of the plant is kept at the Herbarium, Department of Botany, University of Dar es Salaam (L. Mwasumbi = 12761). The description of the plant has been submitted for publication in The Kew Bulletin.

^{1}H NMR (90 MHz, $CDCl_3$): δ 1.60 (*s*, 6H), 1.67 (*s*, 3H) and 1.75 (*s*, 3H) due to 4 × Me groups; 1.90–2.20 (*m*, 8H) due to 4 × allylic CH_2 groups; 3.45 (*br d*, $J = 7$ Hz, 2H: H-1′); 5.19 (*m*, 2H: H-6′ and H-10′); 5.45 (*br t*, $J = 7$ Hz, 1H: H-2′); 6.85 (*br s*, 1H: H-2); 7.0–7.5 (complex *m*, 3H: H-5, H-6 and H-7); 7.6–7.7 (*m*, 1H: H-4) and 7.95 (*br s*, 1H: N–H); CI-MS (CH_4) *m/z* (rel. int.): 321 $[M]^+$ (16); 184 $[M - C_{10}H_{17}]^+$ (10.5); 158 $[184 - CN]^+$ (5.3) and 130 $[M - C_{14}H_{23}]^+$ (100) and ^{13}C NMR resonances as shown in Table 1.

Table 1. Tentative assignment of ^{13}C NMR (15.08 MHz, $CDCl_3$) spectral data for 3-farnesylindole (1)

Chemical shift (δ)	Assignment
136.1	C-8
135.2	C-7′
134.6	C-3′
130.7	C-11′
127.1	C-9
124.0	C-10′
123.8	C-2
122.5	C-6
121.4	C-5
120.7	C-2′
118.7 (*br*)	C-4 and C-6
110.4 (*br*)	C-3 and C-7
38.7 (*br*)	C-4′ and C-8′
25.6 (*br*)	C-12′
25.6 (*br*), 24.5 and 22.7	C-9′, C-5′ and C-1′
16.5	C-3′Me
14.9 (*br*)	C-7′Me and C-11′Me

br = Broad signal.

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REFERENCES

1. Achenbach, H. and Raffelsberger, B. (1979) *Tetrahedron Letters* 2571.
2. Achenbach, H., Renner, C. and Addae-Mensah, I. (1984) *Heterocycles* **22**, 2501.
3. Benesova, V., Samek, Z., Herout, V. and Sorm, F. (1969) *Collect. Czech. Chem. Commun.* **34**, 1807.
4. Plieninger, H. and Sirowei, H. (1971) *Chem. Ber.* **104**, 2027.
5. Ishi, H. and Muzakani, Y. (1975) *Tetrahedron* **31**, 933.
6. Jerram, W. A., McInnes, A. G., Maas, W. S. G., Smith, D. G., Taylor, A. and Walter, J. A. (1975) *Can. J. Chem.* **53**, 727.
7. Gomez, F., Quijano, L., Calderon, J. S., and Rios, T. (1980) *Phytochemistry* **19**, 2202.
8. Crombie, L., King, R. W., and Whiting, D. A. (1975) *J. Chem. Soc. Perkin Trans I*, 913.
9. Johnson, L. F., and Jankowski, W. C. (eds) (1972) "*Carbon*-13 *NMR spectra*". Wiley-Interscience, New York.

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TWO GUAIANOLIDES FROM *CENTAUREA COLLINA*

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Key Word Index—*Centaurea collina*; Compositae; sesquiterpene lactones; guaianolides.

Abstract—Two guaianolides isolated from the aerial parts of *Centaurea collina* were identified as 3β-hydroxy-8α-epoxymethylacriloiloxy-4(15),10(14),11(13)-trien-(1αH),(5αH)-guaian-6,12-olide and its 11β,13-dihydro derivative by spectroscopic methods.

INTRODUCTION

Many sesquiterpene lactones have been reported from the large genus *Centaurea* (Compositae, Cynareae) with approximately 700 species [1]. In the present paper we report the isolation and structure elucidation of two guaianolides from *C. Collina*, one of them being new. In previous work [2–4] several flavonoids were reported from this plant.

RESULTS AND DISCUSSION

From the methanolic extract of the aerial parts of *C. collina*, two sesquiterpene lactones were isolated.

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