was obtained from fraction 16 by repeated prep. TLC on silica gel using cyclohexane–EtOAc–MeOH (10:5:1) and cyclohexane–EtOAc–Me_2CO–MeOH (30:5:10:1) as solvent systems.

Sativanine-G. $C_{28}H_{42}N_4O_5$ ([M]$^+$ 514.3168, calc. for: 514.3181). UV λ_{max} nm: 320 and 258; IR ν_{max} cm^{-1}: 3380 (–NH), 1670, 1635 (*sec.* amide), 2835 (–OMe), 2780 (–NMe), 1610 (>C=C<), 1230 and 1040 (aryl ether); MS: *m/z* 514 [M]$^+$, 457, 401, 400, 374, 304, 259, 233, 216, 209, 165, 114 (base peak), 96, 86. Sativanine-G (3 mg) was hydrolysed with 6 N HCl (10 hr) in a sealed tube. The hydrolysate was evapd to dryness and examined by PC (*n*-BuOH–HOAc–H_2O, 4:1:5). *N,N*-Dimethylisoleucine and isoleucine were identified by comparison with authentic compounds.

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REFERENCES

1. Tschesche, R., Last, H. and Fehlhaber, H.-W. (1967) *Chem. Ber.* **100**, 3937.
2. Tschesche, R., Miana, G. A. and Eckhardt, G. (1974) *Chem. Ber.* **107**, 3180.
3. Tschesche, R., David, S. T., Uhlendorf, J. and Fehlhaber, H.-W. (1972) *Chem. Ber.* **105**, 3106.
4. Tschesche, R., Shah, A. H. and Eckhardt, G. (1979) *Phytochemistry* **18**, 702.
5. Shah, A. H., Pandey, V. B., Eckhardt, G. and Tschesche, R. (1984) *Phytochemistry* **23**, 931.
6. Shah, A. H., Pandey, V. B., Eckhardt, G. and Tschesche, R., *Phytochemistry* (submitted).
7. Nasir, E. and Ali, S. I. (1972) *Flora of West Pakistan*, p. 459.
8. Parker, R. N. (1956) *A Forest Flora of the Punjab with Hazara and Delhi*, p. 83.
9. Tschesche, R., Welters, R. and Fehlhaber, H.-W. (1967) *Chem. Ber.* **100**, 323.

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CANTHIN-6-ONE, UNDULATONE AND TWO QUASSINOIDS FROM *HANNOA KLAINEANA* ROOTS

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Key Word Index—*Hannoa klaineana*; Simaroubaceae; canthin alkaloid; canthin-6-one; coumarin; scopoletin; quassinoids; undulatone; 15-desacetylundulatone; 6α-tigloyloxyglaucarubol.

Abstract—Canthin-6-one, scopoletin, undulatone and two new quassinoids, 15-desacetylundulatone and 6α-tigloyloxyglaucarubol were isolated from *Hannoa klaineana* roots; quassinoids were obtained in high yields from this plant material.

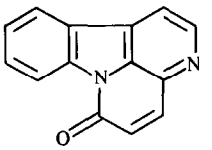
INTRODUCTION

The isolation and identification of seven alkaloids from three different samples of *Hannoa klaineana* Pierre et Engler roots have been reported [1]. Further investigations performed on one sample of the same plant material have led to the isolation and the identification of an eighth alkaloid, canthin-6-one (**1**), a coumarin, scopoletin (**2**) and three quassinoids: undulatone (**3**) firstly isolated from *Hannoa undulata* [2] and two new related compounds, 15-des-acetylundulatone (**4**) previously obtained by chemical hydrolysis of undulatone [2], and 6α-tigloyloxy-glaucarubol (**5**).

RESULTS AND DISCUSSION

A methanolic extract of *H. klaineana* roots was fractionated by column chromatography and the fractions further purified either by reverse phase column chromatography (quassinoids) or by preparative TLC (scopoletin, canthin-6-one). This method was found to be more effective for the isolation of polar quassinoids which are not quantitatively extracted by liquid–liquid partition between aqueous methanol and chloroform.

Canthin-6-one (**1**), scopoletin (**2**) and undulatone (**3**) were identified by UV, IR, ^{1}H NMR, MS and by direct TLC comparison with authentic samples. Canthin-6-one had already been isolated from numerous species of Simaroubaceae [3, 4]. As in the case of compound **3**, the UV absorption of **4** at 225 nm was attributed to the presence of α,β-unsaturated ester and α,β-unsaturated ketone functions. The IR spectrum of **4** showed absorptions at 1730, 1700 and 1670 cm^{-1} indicative of δ-lactone, α,β-unsaturated ester and α,β-unsaturated ketone functions; these data confirmed the interpretation of the UV spectrum and indicated the possible absence from **4** of the acetate function of **3**. The mass spectrum showed a molecular ion at *m/z* 492 and a fragment at *m/z* 392 [M − 100]$^+$; moreover ions at *m/z* 83 (C_5H_7O) and 55 (C_4H_7)



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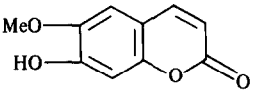

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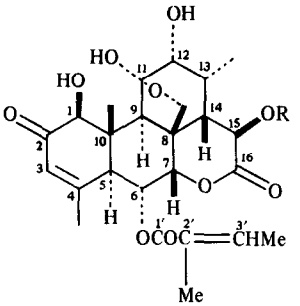

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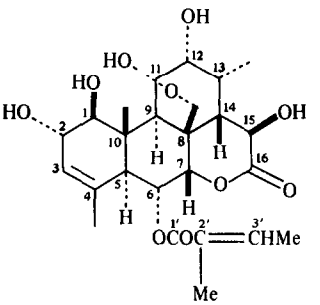
4 R = H



5

suggested esterification by a tiglate moiety; ions characteristic of quassinoids [5] were also observed (*m/z* 135, 151, 247 and 346). From a comparison of the ^{1}H NMR spectral data of compounds **4** and **3**, it was clear that the former differed from the latter only in its lack of a methyl singlet (δ 2.04, Ac) and by the upfield shift of the proton doublet at δ 5.56 to 4.71 (H-15). Finally, the ^{1}H NMR spectrum was found to be identical with that of 15-desacetylundulatone obtained by alkaline hydrolysis of **3** [2].

Compound **5** absorbed UV radiation at 220 nm which suggested that it did not contain an α,β-unsaturated ketone moiety. Its IR spectrum exhibited absorptions at 1720 (δ-lactone), 1700 (α,β-unsaturated ester) and at 1640 cm^{-1} (unsaturated bond). Its ^{1}H NMR spectrum showed one proton multiplet at δ 4.60 related to H-2, one proton doublet at δ 5.45 attributed to H-15; tiglate esterification was further confirmed by mass spectrometry ([M]$^+$, *m/z* 494; [M − 100]$^+$ *m/z* 394, 83 and 55). The presence of a hydroxyl group at C-2 and the correlation between structures **5** and **4** were definitively established by treatment of **5** with pyridinium chlorochromate which afforded compound **4**. This reagent oxidized **5** almost quantitatively within one hour and was more efficient than MnO_2 previously used for the same purpose [6]. Studies on the antitumoral activity of **4** and **5** are in progress.

The high recovery of the quassinoids from *H. klaineana* roots extract compared to the yields recorded for similar quassinoids isolated from other Simaroubaceae species show that the roots of this plant represent an interesting source of quassinoids.

Finally, the differences of chemical composition observed between *H. undulata* and *H. klaineana* invalidate the botanical hypothesis of Nooteboom who considers both species as identical [7].

EXPERIMENTAL

^{1}H NMR: 80 MHz in $CDCl_3$ (compounds **1**–**4**) or at 250 MHz in pyridine-d_5 (compound **5**) using TMS as int. reference; direct inlet, 70 eV.

Plant material. The *H. klaineana* roots sample was collected in the Popular Republic of Congo (Foulakari Falls) in April 1983 and identified by Dr P. Sita botanist at ORSTOM A voucher specimen has been deposited at the National Botanical Garden of Belgium (Meise).

Extraction and separation. Air dried roots (1.5 kg) were first defatted by petrol then extracted with MeOH. CC of the methanolic residue (64 g) on silica gel eluted by $CHCl_3$ containing increasing amounts of MeOH (5 to 50%) afforded 12 fractions. Prep. TLC (silica gel, $CHCl_3$–MeOH, 19.1) of the fractions eluted with 5% MeOH gave 70 mg **1** and 95 mg **2**. The fractions eluted with 5 to 10% MeOH were purified by CC (same conditions as used in the first step) followed by reversed phase CC on a Lichroprep^R RP-8 column (Merck) with EtOH–H_2O to give **3** (600 mg), **4** (900 mg) and **5** (100 mg).

15-Desacetylundulatone (**4**). White needles from MeOH–$C_2H_4Cl_2$ R_f 0.66 (silica gel, $CHCl_3$–MeOH, 17:3, UV λ_{max}^{EtOH} nm: 225, IR ν_{max}^{KBr} cm^{-1}: 3440 *br*, 1730, 1700, 1670; ^{1}H NMR ($CDCl_3$): δ 1.24 (3H, *d*, *J* = 6 Hz, H-13), 1.35 (3H, *s*, H-10), 1.87 (3H, *d*, *J* = 6 Hz, H-3'), 1.88 (3H, *s*, H-2'), 2.04 (3H, *s*, H-4), 2.70 (1H, *s*, H-9), 3.58 (1H, *m*, H-12), 3.78, 4.13 (1H, *d*, *J* = 8 Hz, CH_2O), 4.12 (1H, *s*, H-1), 4.69 (1H, *d*, *J* = 2 Hz, H-7), 4.71 (1H, *d*, *J* = 10 Hz, H-15), 5.56 (1H, *dd*, *J* = 2, 11 Hz, H-6), 6.15 (1H, *s*, H-3), 7.03 (1H, *d*, *J* = 7, H-3'); MS: *m/z* (rel. abundance) 492 [M]$^+$ (6), 474 (23), 392 (13), 374 (35), 356 (74), 346 (33), 328 (33), 252 (73), 247 (47), 187 (75), 151 (55), 135 (37), 100 (97), 83 (95), 55 (100)

6α-Tigloyloxyglaucarubol (**5**) White needles from MeOH–$CHCl_3$ R_f 0.50 (silica gel, $CHCl_3$–MeOH, 17:3). UV λ_{max}^{EtOH} nm: 220; IR ν_{max}^{KBr} cm^{-1}: 3460, 3400, 1720, 1700, 1640; ^{1}H NMR (pyridine-d_5): δ 1.62 (3H, *d*, *J* = 7 Hz, H-13), 1.70 (3H, *d*,

J = 7 Hz, H-3'), 1.88 (3H, *s*, H-10), 1.90 (6H, *s*, H-4 and H-2'), 3.21 (1H, *s*, H-9), 3.48 (1H, *d*, J = 12 Hz, H-5), 4.00, 4.51 (1H, *d*, J = 8 Hz, CH_2O), 4.20 (1H, *m*, H-12), 4.29 (1H, *d*, J = 8 Hz, H-1), 4.60 (1H, *m*, H-2), 4.98 (1H, *d*, J = 2 Hz, H-7), 5.45 (1H, *d*, J = 9 Hz, H-15), 5.82 (1H, *s*, H-3), 5.99 (1H, *dd*, J = 2, 11 Hz, H-6), 7.10 (1H, *d*, J = 7 Hz, H-3'); MS: *m/z* (rel. abundance) 494 $[M]^+$ (0.01), 424 (5), 414 (32), 394 (11), 247 (5), 256 (68), 187 (73), 151 (15), 149 (74), 135 (53), 100 (68), 83 (95), 55 (100).

Hydrolysis of **3**. A soln of **3** (20 mg) in MeOH–H_2O (1 : 1) was maintained at pH 9 at room temp. for 1 hr. After neutralization, the mixture was concd and the reaction products were purified by prep. TLC on silica gel ($CHCl_3$–MeOH, 19 : 1). The more polar 15-desacetylundulatone was isolated (yield 10%) and shown to be identical to **4** by UV, IR, MS and by TLC on silica gel.

Oxidation of **5**. A CH_2Cl_2 soln of pyridinium chlorochromate (10 mg in 1 ml) was added to 1 ml of a saturated CH_2Cl_2 soln of **5** and then stirred at room temp. for 1 hr. The reaction products were then separated by prep. TLC on silica gel ($CHCl_3$–MeOH, 9 : 1); the major product (9 mg) was identical to **4** (TLC on silica gel, UV, IR and MS).

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REFERENCES

1. Luyengi, L. and Vanhaelen, M (1984) *Phytochemistry* **23**, 453.
2. Wani, M. C., Taylor, H. L., Thompson, J. B. and Wall, M. E. (1979) *Tetrahedron* **35**, 17.
3. Lassak, E. C., Polonsky, J. and Jacquemin, H. (1977) *Phytochemistry* **16**, 1126.
4. Ohmoto, T., Koike, K. and Sakamoto, Y. (1981) *Chem Pharm. Bull.* **29**, 390.
5. Fourrey, J. L., Das, B. C and Polonsky, J. (1968) *Org. Mass. Spectrom.* **1**, 819.
6. Polonsky, J. and Bourguignon-Zylber, N. (1965) *Bull. Soc Chim. Fr.* 2793.
7. Nooteboom, H P. (1962) *Blumea* **11**, 509

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ALKALOIDS FROM *HAPLOPHYLLUM SUAVEOLENS*

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Key Word Index—*Haplophyllum suaveolens*, Rutaceae; alkaloids; flindersine; γ-fagarine; kokusaginine; haplophylline.

Abstract—Flindersine, γ-fagarine, kokusaginine and one new alkaloid of the flindersine-type were isolated from the aerial parts of *Haplophyllum suaveolens*. Spectral methods were used to determine the structures of the alkaloids.

INTRODUCTION

A literature survey revealed that new and known quinoline and other types of alkaloids have been isolated from various *Haplophyllum* species and their structures determined [1–8]. In the present study, benzene and chloroform extracts of the arial parts of *Haplophyllum suaveolens* (DC.) G. Don yielded four alkaloids, one of which was a new compound. The main alkaloid of the plant was flindersine (**1**) [1], the second known alkaloid was γ-fagarine (**2**) [2] and the third kokusaginine (**3**) [9] which has also been obtained from various species of Rutaceae. The new alkaloid has an angular pyranoquinoline structure like flindersine.

RESULTS AND DISCUSSION

H. suaveolens yielded three known and a new alkaloid of furoquinoline and angular pyrano-quinoline types. The identity of the known alkaloids was established by spectral comparison with literature data [1, 2, 9–12].

The structure of the new alkaloid named haplophylline (**4**) was determined by means of UV, IR, ^{1}H NMR and mass spectra. The UV spectrum of **4** was similar to that of flindersine (**1**) (see Experimental), but its IR spectrum however, showed an extra carbonyl band at 1720 cm^{-1}. In addition to flindersine peaks the ^{1}H NMR spectrum of **4** showed peaks for a senecioyloxy moiety at δ 1.88 (3H, *d*, J = 2 Hz), 2.2 (3H, *d*, J = 2 Hz), 5.67 (1H, *t*, J = 1 Hz) and a downfield peak for a methylene group at δ 6.37 (2H, *br s*). The lack of an amidic proton (N–H) signal at δ 11.28 indicated that the substitution could only be on the nitrogen atom. The mass spectrum showed the presence of senecioyloxy and methylene groups on the nitrogen atom. The base peak at *m/z* 324 $[M-15]^+$ corresponds to the base peak of **1** $[212\ [M-15]^+]$, the peak at *m/z* 227 $[M-C_6H_9O_2]^+$ shows the flindersine part of the molecule,