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MAJOR TRITERPENES FROM THE RESINS OF *COMMIPHORA INCISA* AND *C. KUA* AND THEIR POTENTIAL CHEMOTAXONOMIC SIGNIFICANCE*

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Key Word Index—*Commiphora incisa*; *C. kua*; Burseraceae; resin; triterpenes; cycloartane; 1α-acetoxy-9,19-cyclolanost-24-en-3β-ol; lanostane; 29-norlanost-8,24-dien-1α,2α,3β-triol; octanordammaranes; chemical taxonomy.

Abstract—The resin obtained from *Commiphora incisa* has yielded two novel triterpenes which have been identified as 1α-acetoxy-9,19-cyclolanost-24-en-3β-ol and 29-norlanost-8,24-dien-1α,2α,3β-triol. No trace could be found of the octanordammaranes previously reported for this species and it now appears that these originate from the closely related *C. kua*.

INTRODUCTION

In previous papers [2, 3] of this series we reported the isolation of three octanordammaranes (e. g. mansumbinone, **1**) and lignans from the resin of a species identified as *Commiphora incisa* Choiv. collected in the Kora National Reserve, Tana River District, Kenya in 1983. More recently we obtained further resin samples from around the settlements of N'gurunit and Ilaut in Marsabit District, northern Kenya. A voucher specimen (Waterman 1118 at Kew) collected from a tree thought to be *C. incisa* and producing a resin identical by TLC to that reported previously as *C. incisa* [2, 3] has now been identified as being of *C. kua* (J. F. Royle) Vollesen (?syn. *C. flaviflora* Engl.) [4, 5]. These two species are generally encountered in the dry seasons in a sterile and leafless state, at which time they are very difficult to differentiate.

Subsequently we have examined *ca* 20 resin samples from Kora and Ilaut. These were all originally assumed to be *C. incisa* but only about half, including some from both localities, were found to have the octanordammaranes as major constituents. It now seems that the true source of these compounds was *C. kua*, a species not previously recognised as a member of the flora of the Kora Reserve [6], and not *C. incisa*. The remaining resin samples, including one from a tree positively identified as *C. incisa* (Mungai and Nyakundi 55 at EA Herbarium, Nairobi), gave a different TLC pattern. In this paper we report on the isolation and identification of two novel triterpenes from this material.

RESULTS AND DISCUSSION

A ground resin sample showing the TLC pattern typical of *C. incisa* was extracted with diethyl ether and the resulting solution chromatographed over a column of silica gel to give two pure compounds.

The minor compound analysed for $C_{32}H_{52}O_3$. Spectroscopic analysis identified it as a cycloartane triterpene with acetoxyl and hydroxyl substituents. The ^{1}H NMR spectrum revealed the acetoxymethine and oxymethine protons as a triplet ($J = 3.1$ Hz) at δ 4.62 and a double doublet ($J = 12.2, 4.4$ Hz) at δ 3.56 respectively, requiring axial acetoxyl and equatorial hydroxyl substituents. Spin decoupling experiments linked these in a $CH(OAc)–CH_2–CH(OH)$ system. Assuming the normal oxygenation at C-3 this required the structure to be either **2** or **3**. A series of NOE experiments supported assignment of structure **2**. Irradiation of the methyl singlet at δ 0.79 (C-4 axial) gave a 3% enhancement of H-2_{ax} and a 1% enhancement of the C-4 equatorial methyl at δ 1.00. Irradiation of the δ 1.00 methyl caused a 6% enhancement of the oxymethine resonance at δ 3.56, which must therefore be at C-3. Finally, acetylation of the hydroxyl group caused appreciable shielding of 4-Me_{eq} but had negligible effect on the cyclopropane protons, again indicative of structure **2**.

The major compound analysed for $C_{29}H_{48}O_3$ suggesting a nortriterpene. The EIMS showed a major fragment at *m/z* 109 indicative of the normal C-17 side-chain of a tetracyclic triterpene. The ^{1}H NMR spectrum showed only seven methyl resonances, two of which were secondary, and the ^{13}C spectrum four olefinic carbons three of which were quaternary suggesting the compound was an 8,24-diene. The ^{1}H NMR spectrum further revealed the presence of three oxymethine protons and these were shown by decoupling experiments to be linked in a $–CH(OH_{ax})–CH(OH_{eq})–CH(OH_{eq})–CH_{ax}(Me)$ system. This requires that the hydroxy groups be placed at C-1,

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* Part 10 in the series 'Chemistry of the Burseraceae'. For Part 9 see ref. [1].

C-2 and C-3 as a 1α,2α,3β-triol and that there is a single equatorial methyl at C-4. On this basis the major compound can be assigned structure **4**. The proposed structure receives support from the EIMS which gave major ions for loss of a single methyl, the elements of water (twice), and the entire C-17 side chain. Further significant ions at *m/z* 291, 277 and 265 can be attributed to loss of ring-D and associated C-13 and C-14 methyls from the tetracyclic nucleus [7].

Acetylation of **4** gave two products identified as the diacetate (**5**) and the triacetate (**6**). The ^{1}H NMR spectra of **5** and **6** were as anticipated, the equatorial 28-Me resonance being shielded by about 0.1 ppm. ^{13}C NMR spectra were obtained for **4**–**6** (Table 1) and compared with published data for the 3β-acetoxy-24-methyl-29-norlanost-8, 25-diene (**7**) [8]. Pronounced variations were seen for the carbons at C-5, C-8, C-9 and C-10 which can be attributed to the additional oxygenation at C-1 and C-2 [9].

The isolation of **2** and **4** from *C. incisa* represent further extensions of the range of tetracyclic triterpene derivatives known to be produced by *Commiphora* species [10]. A-ring oxygenation at C-1 and C-2 has previously been found only among pentacyclic derivatives [11], and **2** and **4** are the first cycloartane and 29-norlanostane derivatives reported from the family.

Table 1. ^{13}C NMR chemical shift values for 29-norlanost-8, 24-dien-1α,2α,3β-triol (**4**), its di- (**5**) and tri- (**6**) acetoxy derivatives and 3β-acetoxy-24-methyl-29-norlanost-8, 25-diene (**7**)

C	4	5	6	7 [8]
1	73.5	73.4	71.9	
2	76.6	75.5	75.0	
3	74.8	73.9	74.1	78.8
4	36.1	35.4	35.3	36.1
5	39.7	39.1	40.6	47.2
6	20.0	19.9	19.9	20.8
7	28.0	27.9	27.9	28.1
8	130.2	130.0	129.9	133.3
9	138.4	138.4	137.6	134.4
10	42.1	42.2	41.6	36.2
11	21.4	21.3	21.1	21.8
12	24.8	24.7	24.8	25.5
13	44.5	44.5	44.4	44.5
14	50.1	50.1	50.0	49.9
15	30.9	30.7	30.8	31.1
16	30.7	30.7	30.6	30.8
17	50.3	50.3	50.3	50.4
18	15.6	15.6	15.7	15.7
19	24.9	24.8	24.6	18.7
20	36.5	36.1	36.1	36.4
21	18.6	18.6	18.5	18.8
22	36.3	36.2	36.2	34.0
23	25.6	25.5	25.7	
24	125.1	125.1	125.1	
25	130.8	130.8	130.7	
26	25.6	25.5	25.5	
27	17.5	17.5	17.5	
28	18.5	18.3	18.3	20.2
30	14.9	14.7	14.7	15.1
Ac		20.9	20.7	21.3
		20.8	20.7	
			20.7	
		170.5	170.4	170.8
		170.2	170.4	
			170.2	

All spectra run in $CDCl_3$.

EXPERIMENTAL

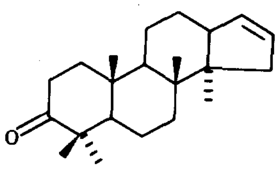
Mps: uncorr. IR: KCl discs. OR measured at 25°. NMR: $CDCl_3$ with TMS as int. standard, ^{1}H spectra run at 360 MHz and ^{13}C spectra at 90.56 MHz. EIMS: 70 eV, direct probe insert between 120 and 150°. Petrol refers to the bp 60–80° fraction.

Plant material. The resin sample used for extraction was collected near Ilaut, Marsabit District on 18/3/1985 (code IP4) and was identical by TLC to a small sample (KO-37) collected in the Kora National Reserve and identified as deriving from *C. incisa* (Mungai and Nyakundi 55, EA Herbarium, Nairobi).

Extraction and isolation of triterpenes. Ground resin (77 g) was extracted with Et_2O and the resulting soln concd to give a yellow gum (40 g) half of which was chromatographed over a column of silica gel. Elution with petrol containing 5% EtOAc gave **2** (5 mg) and with 20% EtOAc gave crude **4** which was pptd with MeOH to give pure **4** (2 g).

1α-*Acetoxy*-9,19-*cyclolanost*-24-*en*-3β-*ol* (**2**). Amorphous solid from petrol: EtOAc. ^{1}H NMR: δ0.43, 0.73 (2H, 2 × *d*, $J = 4.8$ Hz, H-19), 0.79 (3H, *s*, Me-29), 0.86 (3H, *d*, $J = 6.5$ Hz, Me-21), 0.90, 0.91(2 × 3H, 2 × *s*, Me-18, Me-30), 1.00 (3H, *s*, Me-28), 1.59, 1.67 (2 × 3H, 2 × *s*, Me-26, Me-27), 1.74 (1H, *ddd*, $J = 14.0$, 12.2, 3.1 Hz, H-2_{ax}), 2.00 (1H, *ddd*, $J = 14.0$, 4.4, 3.1 Hz, H-2_{eq}), 2.04 (3H, *s*, OAc), 3.56 (1H, *dd*, $J = 12.2$, 4.4 Hz, H-3_{ax}), 4.62 (1H, *t*, $J = 3.1$ Hz, H-1_{eq}), 5.08 (1H, *br t*, $J = 7.2$ Hz, H-24). Found: $[M]^+$ 484.3909; $C_{32}H_{52}O_3$ requires 484.3916. EIMS *m/z* (rel. int.): 484 (17), 424 (100), 409 (31), 406 (38), 391 (11), 311 (15), 285 (12), 219 (10), 205 (14), 201 (19). Compound **2** (5 mg) dissolved in pyridine (1 ml) was treated with Ac_2O (0.2 ml) at room temp. overnight. Normal work-up gave the corresponding diacetate (quantitative yield) as a gum, $[\alpha]_D$ + 31° ($CHCl_3$; *c* 0.05). ^{1}H NMR: δ0.44, 0.75 (H-19), 0.85 (Me-21), 0.86, 0.87 (Me-28, Me-29), 0.90, 0.91 (Me-18, Me-30), 1.59, 1.67 (Me-26, Me-27), 1.79 (H-2_{ax}), 1.96 (H-2_{eq}), 2.02, 2.07 (2 × AcO), 4.63 (H-1_{eq}), 4.88 (H-3_{ax}), 5.08 (H-24). Found: $[M]^+$ 526.4032; $C_{34}H_{54}O_4$ requires 526.4022.

29-*Nor-lanost*-8, 24-*dien*-1α,2α,3β-*triol* (**4**). Amorphous, $[\alpha]_D$ + 38.2° ($CHCl_3$; *c* 0.1). IR ν_{max} cm^{-1}: 3400, 1470, 1375, 1075, 1040. ^{1}H NMR: δ0.70 (3H, *s*, Me-18), 0.90 (3H, *s*, Me-30), 0.91 (3H, *d*, $J = 5.3$ Hz, Me-21), 0.97 (3H, *s*, Me-19), 1.01 (3H, *d*, $J = 5.9$ Hz, Me-28), 1.59, 1.67 (2 × 3H, 2 × *br s*, Me-26, Me-27), 3.30 (1H, *t*, $J = 9.5$ Hz, H-3_{ax}), 3.60 (1H, *dd*, $J = 9.5$, 2.9 Hz, H-2_{ax}), 3.90 (1H, *d*, $J = 2.9$ Hz, H-1_{eq}), 5.08 (1H, *br t*, $J = 6.4$ Hz, H-24). ^{13}C NMR see Table 1. Found: $[M]^+$ 444.3620; $C_{29}H_{48}O_3$ requires 444.3603. EIMS *m/z* (rel. int.): 444 (100), 429 (96), 426 (6), 411 (14), 408 (8), 393 (8), 291 (2), 277 (5), 265 (5), 109 (21). Treatment of **4** (120 mg) in pyridine (4 ml) with Ac_2O (1 ml) at room temp. gave, on normal work-up, 30 mg of 2α,3β-diacetoxy-29-norlanost-8,24-dien-1α-ol (**5**) as a clear gum. IR ν_{max} cm^{-1}: 1735. ^{1}H NMR: δ0.71 (Me-18), 0.90, 0.92 (Me-28, Me-21), 0.93 (Me-30), 1.08 (Me-19), 1.60, 1.68 (Me-26, Me-27), 2.04, 2.08 (2 × OAc), 3.99 (H-1), 5.07 (H-3), 5.08 (H-24), 5.15 (H-2). ^{13}C NMR see Table 1. Found: $[M]^+$ 528.3737; $C_{33}H_{52}O_5$ requires 528.3815. Treatment of **4** (1 g) in pyridine (20 ml) with Ac_2O (5 ml) under reflux for 5 hr gave, after normal work-up, 600 mg of 1α,2α,3β-triacetoxy-29-norlanost-8,24-diene (**6**). IR ν_{max} cm^{-1}: 1740. ^{1}H NMR: δ0.66 (Me-18), 0.83 (Me-30), 0.87, 0.90 (Me-21, Me-28), 1.12 (Me-19), 1.57, 1.65 (Me-26, Me-27), 1.91, 2.00, 2.01 (3 × OAc), 4.92 (H-3), 5.08 (H-2, H-24), 5.31 (H-1). ^{13}C NMR see Table 1. Found: $[M]^+$ 570.3923; $C_{35}H_{54}O_6$ requires 570.3920.



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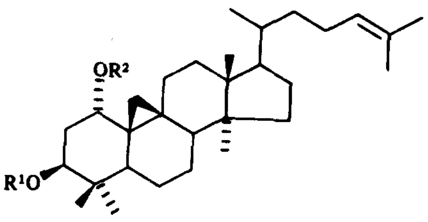
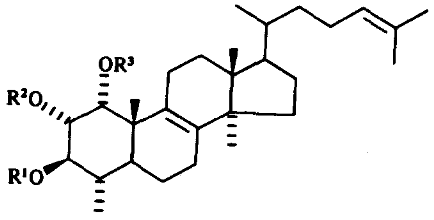
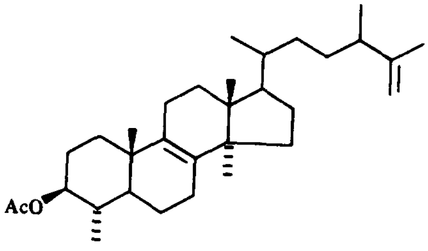


	R¹	R²
2	H	Ac
3	Ac	H



	R¹	R²	R³
4	H	H	H
5	Ac	Ac	H
6	Ac	Ac	Ac



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