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LIMONOIDS FROM *NYMANIA CAPENSIS*

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Key Word Index—*Nymania capensis*; Meliaceae; limonoids; prieurianin.

Abstract—The bark and timber of *Nymania capensis* contain prieurianin and other complex limonoids, four of which have been identified. The chemical evidence serves to support the taxonomic position of *Nymania* in the family Meliaceae.

INTRODUCTION

Nymania capensis S.O. Lindb. is a small tree found in drier parts of South Africa. It is well known for the inflated pink calyces which surround the ripe fruit, giving the common name of Christmas Bells. The taxonomic position of this plant has been much disputed, but it is now considered to belong to the Meliaceae, where it is placed in the tribe Turraeeae. [1]. This tribe is little known chemically. *Naregamia alata* [2] does not contain any limonoids, while *Turrea floribunda* [Connolly, J. D. and Taylor, D. A. H., unpublished work] contains limonoids with structures of the simple *Trichilia* type, related to heudelottin and havanensin. No other genera have been investigated chemically.

RESULTS AND DISCUSSION

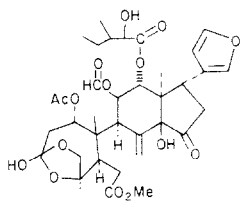
We have now investigated the timber, bark and seed of *Nymania capensis* and find the plant to be a rich source of limonoids of the more complex *Trichilia* type. The bark and timber yielded crystalline prieurianin (**5**) [3] and the mother liquors from the crystallization gave a complex mixture. As is common with this type of extract, separation was a major problem, probably partly owing to isomerization during chromatography [4–5]. A combination of CC, prep. TLC, and HPLC on a reversed-phase column gave four pure substances, which we name as Nymania compounds **1–4**. The structure elucidation was mainly based on ^{13}C NMR spectroscopy; attempted chemical degradation of these complex substances generally led to mixtures which were very difficult to resolve. The seed, like that of *Entandrophragma* species, was very bitter but failed to yield limonoids. The cause of the bitter taste is not known in either case.

Nymania **1** was isolated by chromatography on Si gel columns. It remained amorphous, but gave a crystalline diacetate, $C_{40}H_{52}O_{17}$; the NMR spectra were very similar to those of prieurianin, the differences showed that **1** lacked the primary acetate at C-29 and instead of a lactone carbonyl at C-1 an *ortho* ester was indicated by the characteristic carbon resonance at δ 119.5. We have previously obtained similar *ortho* esters by partial hydrolysis of natural products [6]. We therefore assign to this compound the structure **1**. The diacetate was acylated on the tert. hydroxyl at C-3, and in the C-12 side-chain ester.

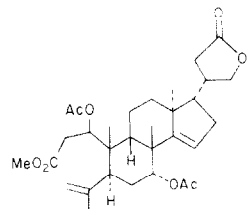
Nymania **2** was isolated as a crystalline solid, $C_{31}H_{44}O_8$, after chromatography on Si gel columns. The ^1H NMR and ^{13}C NMR spectra contained bands indicating the presence of two acetates, a carbomethoxy group, an isopropenyl group, a second trisubstituted double bond and a lactone. There was no furan ring and the spectra suggested it was replaced by a 3-substituted butyrolactone. There was no characteristic UV absorption, so the double bonds were not conjugated. The structure was elucidated by proton decoupling at high field, which enabled the identification of a chain of coupled protons from C-21 in the lactone to the double bond at C-15, and of an isolated CH_3–OOC–CH_2–CHOAc group. These features seem to be uniquely accommodated by the structure **2**. This type of opened ring A is not common, but was discovered in canaric acid [7], and may occur in methyl senegalensate [8]. We no longer have any methyl senegalensate to test this hypothesis.

The third and fourth compounds which were both amorphous, were separated from a column fraction by HPLC. The first of these, $C_{31}H_{38}O_{10}$, showed spectral features, listed in the Experimental section, consistent with the structure **3** which we assign to it, while the other, $C_{33}H_{42}O_{12}$, appeared to be the corresponding saturated acetoxy lactone **4**.

These compounds isolated from *Nymania* are completely typical of those which we have isolated from species of the genera *Guarea*, *Trichilia* and *Aphanamixis*, and strongly support the placing of *Nymania* in the subfamily Melioideae of the Meliaceae. Not enough is yet known of the chemistry of the tribe Turraeeae to comment on the location of *Nymania* in this tribe, but the chemistry of *Turrea floribunda*, the one other species known to contain limonoids, is consistent with the suggested relationship.



1



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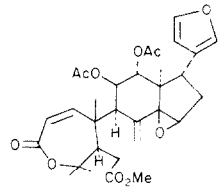

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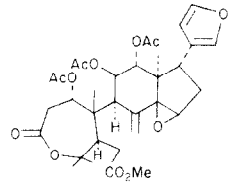

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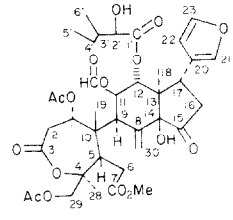

5

Preiurianin and related compounds present some interesting stereochemical problems, associated with steric crowding around the C-9:C-10 bond. Thus in some compounds there is free rotation about this bond, leading to sharp NMR spectra at room temperature, while in others there is restricted rotation [3]. Some C-29 alcohols form hemi *ortho* esters, like Nymania **1**, while others like rohituka compound 1 do not [4]; and the C-14-hydroxyl group adds to C-1 in some unsaturated lactones like polystachin [9], while in others such as rohituka compound 7 [4] it does not. An analysis of the last of these three cases has been presented [9], in terms of preferred conformations of the molecules.

EXPERIMENTAL

Ground bark of *Nymania capensis* (800 g collected in the Outeniqua Mountains near Oudtshoorn, herbarium specimen DAHT 308 at Oxford) was extracted with refluxing *iso*-hexane. The precipitate (20 g) which formed was collected and chromatographed on a Si gel column, yielding after crystallization prieurianin (0.5% yield from the bark), identical with an authentic specimen, and a mother liquor. Further separation of the latter gave small amounts of the following compounds, the yields reflect the difficulty of separation rather than the quantity present. The timber gave a similar extract in about one-tenth the yield. ^{1}H NMR spectra are collected in Table 1.

Nymania **1** was obtained as a gum by chromatography on Si gel. ^{13}C NMR: 206.6*s*, 175.6*s*, 174.6*s*, 169.7*s*, 160.9*d*, 142.8*d*, 140.5*d*, 138.9*s*, 126.0*t*, 123.3*s*, 119.5*s*, 110.7*d*, 82.6*s*, 80.9*s*, 74.7*d*, 74.2*d*, 73.5*t*, 71.4*d*, 71.0*d*, 52.7*q*, 50.7*d*, 49.4*s*, 49.0*d*, 48.7*s*, 41.6*t*, 38.1*d*, 38.1*t*, 35.3*d*, 33.5*t*, 28.5*q*, 23.3*t*, 20.8*q*, 16.7*q*, 15.1*q*, 12.9*q*, 11.4*q*.

The diacetate of **1** had $[M]^+$ at *m/z* 804.3207, $C_{40}H_{52}O_{17}$ requires 804.3201; ^{13}C NMR: 207.0*s*, 175.6*s*, 170.1*s*, 169.7*s*, 168.9*s*, 167.5*s*, 161.5*d*, 143.1*d*, 141.0*d*, 138.5*s*, 126.3*t*, 123.2*s*, 121.0*s*, 110.7*d*, 85.5*s*, 81.2*s*, 76.0*d*, 74.2*d*, 73.8*t*, 72.2*d*, 71.2*d*, 53.0*q*, 50.7*d*, 49.5*s*, 49.5*d*, 49.2*s*, 41.8*t*, 39.2*t*, 36.2*t*, 35.4*d*, 34.1*t*, 26.7*q*, 24.4*t*, 22.0*q*, 21.2*q*, 20.6*q*, 16.5*q*, 15.4*q*, 13.1*q*, 11.4*q*; mp 249°; $[\alpha]_{18}^{D} - 42°$.

Nymania **2** also obtained from Si gel column, had mp 213°, $[\alpha]_{18}^{D} - 23°$. $[M]^+$ at *m/z* 544.3039, $C_{31}H_{44}O_8$ requires 544.3036; ^{13}C NMR: 176.5*s*, 171.7*s*, 170.2*s*, 169.8*s*, 158.9*s*, 144.9*s*, 118.9*d*, 116.4*t*, 76.6*d*, 74.4*d*, 72.4*t*, 58.3*d*, 52.0*q*, 46.3*s*, 44.2*s*, 44.1*d*, 42.4*s*, 37.5*d*, 35.4*t*, 34.7*t*, 34.4*d*, 34.0*t*, 34.0*t*, 29.2*t*, 26.8*q*, 22.8*q*, 21.2*q*, 21.0*q*, 20.0*q*, 18.1*t*, 15.0*q*.

Table 1. ^{1}H NMR spectra of Nymania compounds (chemical shift in ppm from internal TMS, couplings in Hz, J for doublets, $W_{1/2}$ for multiplets)

	Nymania 1*	Nymania 2	Nymania 1 acetate*	Nymania 3*	Nymania 4*
H-1	5.21 *m*	5.48(*dd* 2, 10)	5.33 *m*	6.28(*d* 13)	5.67
H-2A	—†	2.81(*dd* 2, 14)	—	6.95	3.24
H-2B	—	2.42(*dd* 10, 14)	—	NA‡	—
H-5	—	—	—	3.88(*m* 10.7)	—
H-6A	—	2.16(*m* 15, 12, 3)	—	2.32	—
H-6B	—	1.66(*m* 15, 4, 4)	—	—	—
H-7	NA	5.16 (*m* 3, 4)	NA	NA	NA
H-9	4.25 (*d* 4.9)	—	4.33(*d* 7)	3.12(*d* 6.7)	3.53(*d* 6.9)
H-11	5.42 *m*	—	5.28 *m*	5.6 *m*	5.45 *m*
H-12	6.08(*d* 10.9)	—	6.09(*d* 11)	5.91(*d* 11.1)	5.71(*d* 10.1)
H-15	—	5.29(*m* 2, 4)	—	3.91	3.78
H-16A	—	2.18(*m* 4, 7, 15)	*ca* 2.46	*ca* 2.13	—
H-16B	—	2.03(*m* 2, 11, 15)	—	—	—
H-17	4.03(*m* 18)	1.71(*m* 5, 7, 11)	4.05 *m*	3.07(*m* 16.8)	2.96 *m*
H-20	NA	2.72(*m* 48)	NA	NA	NA
H-21A	7.26	4.46(*m* 8.5, 8.5)	7.43	7.36	7.35
H-21B	NA	3.93(*m* 8.5, 11.5)	NA	NA	NA
H-22A	6.30	2.52(*dd* 8.5, 17)	6.37	6.20	6.19
H-22B	NA	2.21(*dd* 11.5, 17)	NA	NA	NA
H-23	7.41	NA	7.43	7.16	7.15
H-29A	4.15(*d* 8)	5.04(*m* 3)	4.17(*d* 8)	NA	NA
H-29B	3.65	4.86 *br s*	3.83	NA	NA
2H-30	6.10, 5.04	—	6.07, 6.03	5.39, 5.26	5.20, 5.48
CO_2Me	3.78	3.67	3.79	3.75	3.68
OAc	2.07	2.04, 1.99	2.19, 2.13, 2.11	2.15, 1.76	2.11, 2.11, 1.81
CMe	1.5	1.79 *br s*	1.54	1.59	1.64
	1.37	1.15	1.37	1.33	1.60
	1.1	1.02	1.08	1.04	1.41
		0.97		0.95	0.95
O·CHO	7.99	NA	8.02	NA	NA
H-2′	—	NA	4.70(*d* 4)	NA	NA

*Determined in $CDCl_3$ at 30° on a CFT20 spectrophotometer at 80 MHz.
†, Not recorded.
‡NA, Not applicable.

Nymania **3** obtained by HPLC, was a gum. $[M]^+$ at m/z 570.2464, $C_{31}H_{38}O_{10}$ requires: 570.2463; ^{13}C NMR: 173.5*s*, 170.3*s*, 169.7*s*, 166.6*s*, 148.5*d*, 142.5*d*, 140.4*d*, 136.9*s*, 122.3*s*, 122.3*d*, 120.9*t*, 111.2*d*, 83.6*s*, 74.4*d*, 71.1*s*, 71.1*d*, 59.6*d*, 53.4*q*, 52.3*d*, 50.1*d*, 46.3*s*, 45.2*s*, 38.0*d*, 35.0*t*, 33.5*t*, 30.3*q*, 22.7*q*, 22.4*q*, 20.4*q*, 20.3*q*, 13.5*q*.

Nymania **4**, obtained similarly, was also a gum. $[M]^+$ at m/z 630.2676, $C_{33}H_{42}O_{12}$ requires: 630.2676; ^{13}C NMR: 173.7*s*, 170.8*s*, 170.2*s*, 170.2*s*, 170.8*s*, 142.6*d*, 140.4*d*, 135.0*s*, 123.7*s*, 122.3*t*, 111.3*d*, 84.6*s*, 75.1*s*, 72.1*d*, 71.4*d*, 71.4*d*, 71.2*s*, 59.7*d*, 52.1*q*, 51.8*d*, 50.0*d*, 45.3*s*, 45.0*s*, 38.2*d*, 35.8*d*, 35.0*d*, 33.5*t*, 29.7*q*, 24.6*q*, 21.3*q*, 21.0*q*, 20.7*q*, 18.2*q*, 13.4*q*.

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