Notholaena Terpenoids: Two New Epimeric Diterpenes from the Frond Exudate of the Fern, *Notholaena rigida*

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From the farinose frond exudate of the fern *Notholaena rigida* two new triterpenes have been identified. They were found to be the C-24 epimers of 12β-acetoxy-24, 25-diO-isopropylidene-dammarane-3β, 20(*S*),24,25-tetra-ol. A survey of all triterpenes found in *Notholaena* is presented.

Introduction

In recent papers we reported two pairs of new epimeric isopropylidene-damarane type triterpenes (**XI A, B; XII A, B)** from the frond exudate of the fern *Notholaena rigida* Dav. (Arriaga *et al.*, 1996a, b). Related new epoxy-dammaranes (**I, II**) and an isopropylidene-cyclolanostanol (**V**) were also described from the same species (Arriaga-Giner *et al.*, 1991, 1992). In addition to these previously reported terpenoids, we have now isolated two minor triterpenes (**XIII A, B**) from some remaining fractions. They were identified by detailed NMR spectroscopic studies.

Material and Methods

Collection data for *Notholaena rigida* as well as isolation and analysis procedures are the same as reported earlier (Arriaga-Giner *et al.*, 1991). A fraction previously obtained from this exudate material was subjected to "flash" chromatography on Si-gel using CH_2Cl_2-MeOH 30:1 as eluent. Mass spectra were measured on a VG Autospec at 70 eV *via* solid probe. NMR spectra were recorded on a Bruker AC-300 spectrometer at 300 MHz (for ^1H) and 75.4 MHz (for ^{13}C) in $CDCl_3$ solutions. Multiplicities were assigned through DEPT experiments.

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Two pure products were obtained which appear as colourless oils. They exhibit the following spectral properties:

Compound **XIII A**, (R_f 0.27): EI-MS *m/z* (rel. int.): 576 (M^+, -), 561 (M^+-Me, 0.5), 543 (M^+-Me-H_2O, 4), 525 (M^+-Me-2H_2O, 1) 500 (3), 482 (2), 440 (9), 423 (5), 369 (4), 341 (13), 207 (18), 201 (11), 191 (13), 189 (17), 161 (15), 147 (24), 143 (89), 129 (100), 121 (25), 107 (30), 95 (29), 81 (35), 71 (49) and 59 (88). ^1H NMR δ ppm (*J*, Hz): 0.78, 0.87, 0,96, 0.98, 1.02, 1.12, 1.13, 1.29, 1.36, 1.43, 2.05 (3H each, all s), 3.21 (H-3, dd, 11.1, 5.1), 3.70 (H-24, brd, 8.1) and 4.73 (H-12, ddd, 10.5, 10.5, 5.4). ^{13}C NMR: δ ppm 38.8 (C-1), 27.2 (**a**), 78.6 (C-3), 38.9 (C-4), 55.7 (C-5), 18.1 (C-6), 34.5 (C-7), 39.7 (C-8), 50.0 (C-9), 37.1 (C-10), 28.2 (C-11), 76.6 (C-12), 44.9 (C-13), 52.7 (C-14), 31.5 (C-15), 27.0 (**a**), 52.7 (C-17), 15.3 (**b**), 16.1 (**b**), 73.6 (C-20), 26.2 (**c**), 33.4 (C-22), 23.5 (C-23), 84.3 (C-24), 80.3 (C-25), 22.9 (C-26), 26.0 (**c**), 27.9 (C-28), 15.5 (**b**), 17.3 (C-30), 106.5 [**C**-(OCH_3)$_2$], 28.6 [C-(O**C**H_3)$_2$], 26.9 (**c**), 169.5 (CH_3**C**=**O**) and 21.5 (**C**H_3C=O).

Compound **XIII B**, (R_f 0.24): EI-MS *m/z* (rel. int.): 576 (M^+, -), 561 (M^+-Me, 1), 543 (M^+-Me-H_2O, 2), 525 (M^+-Me-2H_2O, 2) 500 (2), 482 (2), 440 (5), 423 (5), 341 (10), 207 (17), 201 (16), 191 (13), 189 (23), 161 (18), 147 (29), 143 (100), 129 (83), 121 (31), 107 (40), 95 (38), 81 (46), 71 (53) and 59 (88).^1H NMR δ ppm (*J*, Hz): 0.78, 0.86, 0,96, 0.99, 1.02, 1.14, 1.14, 1.26, 1.36, 1.43, 2.06 (3H each, all s), 3.21 (H-13, dd, 11.1, 4.8), 3.68 (H-24, dd, 8.4, 3.1) and 4.74 (H-12, ddd, 9.6, 9.6, 4.8). ^{13}C

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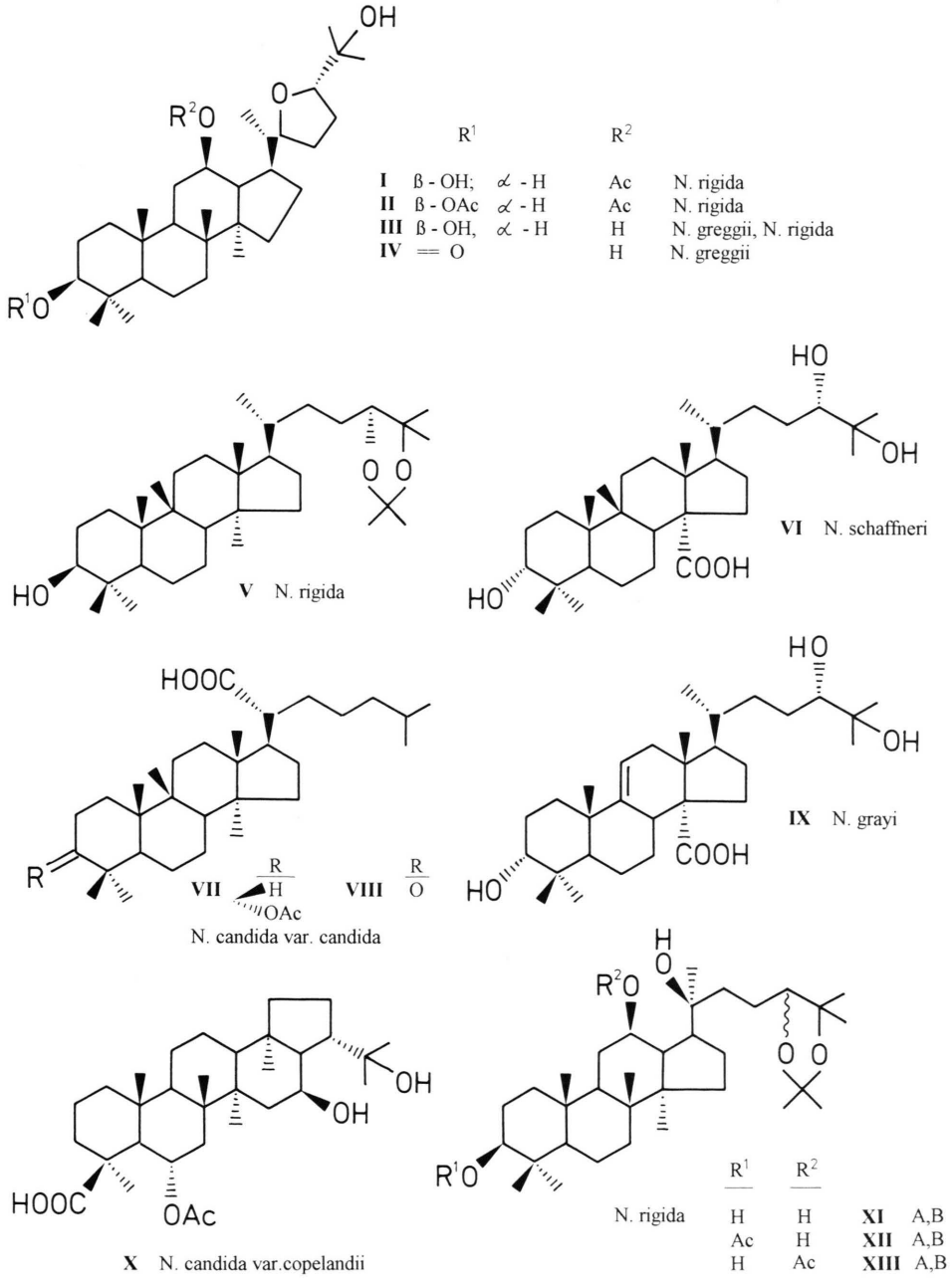
NMR: δ ppm 38.8 (C-1), 27.2 (**a**), 78.6 (C-3), 38.9 (C-4), 55.8 (C-5), 18.2 (C-6), 34.5 (C-7), 39.7 (C-8), 50.0 (C-9), 37.1 (C-10), 28.2 (C-11), 76.3 (C-12), 45.0 (C-13), 52.6 (C-14), 31.5 (C-15), 27.2 (**a**), 52.6 (C-17), 15.3 (**b**), 16.1 (**b**), 73.4 (C-20), 26.4 (**c**), 33.0 (C-22), 23.6 (C-23), 84.0 (C-24), 80.3 (C-25), 22.9 (C-26), 26.2 (**c**), 27.9 (C-28), 15.4 (**b**), 17.4 (C-30), 106.5 [**C**-$(OCH_3)_2$], 28.5 [C-$(O\mathbf{CH_3})_2$], 26.9 (**c**), 169.7 ($CH_3\mathbf{C}$=**O**) and 21.5 ($\mathbf{CH_3}$C=O). Assignments marked with (a,b,c) are interchangeable.

Results and Discussion

The ^{1}H NMR spectra of compounds **XIII A/B** are very similar exhibiting eleven methyl signals



(all singlets) one of them arising from an acetoxy group. Three sets of deshielded one-proton resonances between 3.5–4.4 ppm correspond to methine hydrogens adjacent to an oxygen substituent. Based on their splitting pattern and followed from the lack of the peak at *m/z* 249 in the MS spectra, a 12β-acetoxy substituent is assumed, the two other signals corresponding to the 3β-hydroxy group and an ether linkage.

The ^{13}C NMR spectra display 35 carbon atom signals, showing five deshielded carbons between 73.4–84.3 ppm, a carbon signal at 106.5 ppm that suggested the existence of an acetonide and a carbonyl (c.a. 170 ppm).

Comparison of the NMR spectra of compounds **(XIII A, B)** showed no differences with previously isolated triterpene-pentol epimers (Arriaga-Giner *et al.*, 1996a, b) other than affecting the neighbourhood of the acetate. The chemical shifts for the signals attributed to C-17, C-21 and C-22 suggested the same stereochemistry at C-20 (Asakawa *et al.*, 1977). Thus, both compounds appear to be epimers at C-24. The structure of these new natural products is fully in accordance with 12β-acetoxy-24,25-di-O-isopropylidene-dammarane-3β,20(*S*),24,25-tetra-ol, but assignment of the two epimers at C-24 was not possible.

Three pairs of C-24 epimers of isopropylidene derivatives of the same dammarane triterpenoids have been isolated from *N. rigida* (**XI – XIII**), all having the same substitution pattern and differing in the location of the acetyl group. Furthermore, two related dammaranes with cyclic side-chain (**I**, **II**) and a cyclolanostane (**V**) have been reported for this species. Pyxinol (**III**), the only previously reported product, has been found in both, *N. rigida* (Arriaga *et al.*, 1996 b) and *N. greggii* (Appendino *et al.*, 1992). The latter species also afforded the related new dammarane-ketone (**IV**) (Appendino *et al.*, 1992). Cyclolanostan-triterpene acids (**VI – VIII**) have been isolated from *N. schaffneri* and *N. candida* var. *candida* (Arriaga-Giner *et al.*, 1992a), while *N. grayi* (Arriaga-Giner *et al.*, 1992b) and *N. candida* var. *copelandii* (Arriaga-Giner *et al.*, 1986) yielded dammarane and hopane triterpene acids, **IX** and **X**, respectively. *N. neglecta* afforded the trivial triterpene lupeone.

Apart from lupeone, the triterpenoids isolated from leaf exudates of the genus *Notholaena* are usually highly oxygenated. They are new natural products, except for lupeone and pyxinol (Arriaga *et al.*, 1996b). The latter was previously isolated from the lichen *Pyxine endochrysina* (Yosioka *et al.*, 1972).

Acetonides as natural products are rather unusual. It is striking that we have found seven of these rare derivatives in *N. rigida*.

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