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PTEROCARPANS OF *NEORAUTANENIA EDULIS* AND *N. AMBOENSIS*

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Key Word Index—*Neorautanenia edulis*; *N. amboensis*; Leguminosae; root bark; pterocarpans; structural determination.

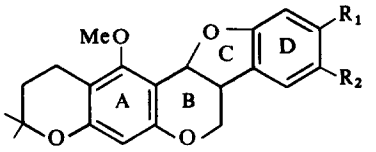
Abstract—The root bark of *Neorantanenia edulis* and *N. amboensis* yielded six new natural pterocarpanoids, the structures of which have been determined mainly by physical methods and by partial syntheses. They include edulane, edudiol, neoraucarpan, neorautanin, edulenol, and neoraucarpanol.

INTRODUCTION

Our interest in the phytochemical examination of the family *Neorautanenia* was stimulated by the isolation of a number of 12a-substituted rotenoids [1] and related compounds [2]. Our continued examination of the extractives of the root bark of *N. edulis* and *N. amboensis* led to the isolation of trace quantities of six new pterocarpanoid compounds. We now report upon their structural elucidation and on their plausible interrelationships.

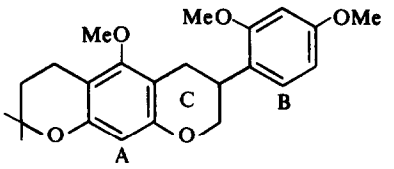
RESULTS AND DISCUSSION

The MS of the isolated compounds are compatible with those previously reported for pterocarpans [3]. Their heterocyclic protons are represented by the characteristic four-spin system in PMR spectra [4]. Their IR spectra lack carbonyl absorption, but contain several prominent aryl ether bands [5]. Compounds (**5**), (**6**) and (**9**) also give positive Labat reactions, indicating the presence of methylenedioxy-groups [6].



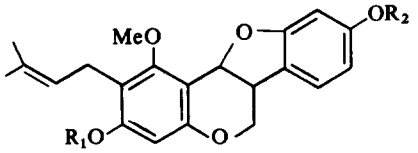
(**1**) R_1 = OMe; R_2 = H
(**6**) $R_1 + R_2 = OCH_2O$

Compound (**1**), edulane, $C_{22}H_{24}O_5$ (M^+ 368), gives a purple-red colour with $HClO_4/FeCl^3$. The PMR spectrum includes signals from two OMe groups, two 2-proton triplets at τ 8.24 and 7.23 (H-3′ and H-4′, J 6.5 Hz), a 6-proton singlet at τ 8.65 (*gem*-CMe_2 group of a 2,2-dimethylchromane moiety), and in the aromatic region an ABX system (3H) and singlet (1H) at τ 3.75. In the absence of carbonyl absorption the two remaining O atoms represent ether linkages. Accordingly the remaining signals could be assigned to the heterocyclic protons of a pterocarpan, and the arrangement of the substituents as in (**1**) was determined as follows. Hydrogenolysis of edulane over palladium and subsequent methylation gave the isoflavan (**11**), the five ring C protons showing the characteristic ABMXX′ signals [3] in the PMR spectrum. The MS of this compound displayed typical RDA fragmentation [3] with major peaks at *m/e* 384 (M^+, 73), 220(19), 164(100) and 151(28). The formation of



(**11**)

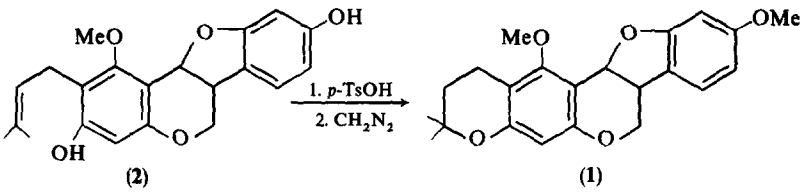
(**12**) shows that ring B contains two OMe groups and hence that ring A contains the remaining OMe group and 2,2-dimethylchromane moiety. The substitution in edulane (**1**) is accordingly assigned as in rings A and D. The position of the single proton of ring A was determined by comparison of its PMR signal with the calculated chemical shift values of Ballantine and Pillinger [7]. The observed signal at τ 3.75 places the proton at C-4 showing that edulane is 2′,2′-diMe-2,3:5′,6′-chromane-1,9-dimethoxypterocarpan.



(**2**) $R_1 = R_2$ = H
(**3**) $R_1 = R_2$ = Me
(**4**) $R_1 = R_2$ = COMe
(**7**) R_1 = H; R_2 = Me
(**8**) R_1 = COMe; R_2 = Me

Edudiol (**2**), $C_{21}H_{22}O_5$ (M^+ 354), is phenolic, as evidenced by positive reaction with $FeCl_3$ and diazotized *p*-nitroaniline. It gives an intense red colour when sprayed with $HClO_4/FeCl_3$. OH-stretching absorption (ν_{max}^{KBr} 3385 cm^{-1}) is present in the IR spectrum. Reaction with CH_2N_2 affords a trimethylated product (**3**) (M^+ 382), and reaction with Ac_2O produced a diacetate (**4**) (M^+ 396). Neither product retained any phenolic character. The chemical shifts in the aromatic region reveal a

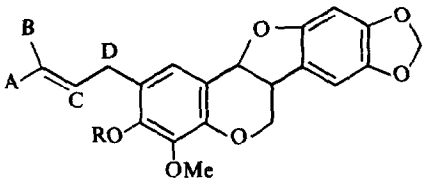
similar oxygenation pattern to that of edulane. The loss of isobutene ($M^+ - 55$) in the MS was indicative of the presence of an *o*-(3.3-dimeallyl)phenol [8]. Chemical proof for this was obtained by interconversion of edudiol (2) and edulane (1) according to Scheme 1. The downfield shift ($\Delta\tau$, 0.17) of the signal at τ 3.70 attributed to 4-H on acetylation [9] is evidence that edudiol is 1-methoxy-2-isopentenyl-3,9-dihydroxypterocarpan.



(2) (1)

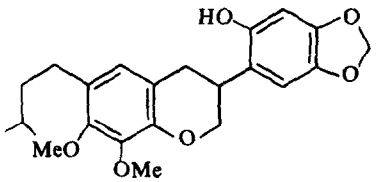
Scheme 1.

Neoraucarpan (5), $C_{23}H_{24}O_6$ (M^+ 396), gives the positive Labat test for a methylenedioxy-group but unlike compounds (1) and (2) it affords a brown-yellow colour with $HClO_4/FeCl_3$. A hydroxydimethoxyisoflavan (13) was obtained by hydrogenolysis and the MS



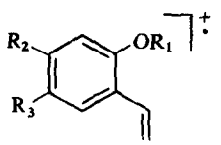
(5) R = Me
(9) R = H
(10) R = COMe

of this compound exhibited only three major peaks, the M^+ at *m/e* 400(60), 343(46, $M^+ - C_4H_9$), and the base peak (14) at 164 arising from RDA cleavage. Hence



(13)

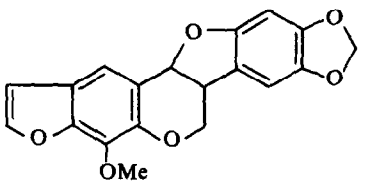
ring A of neoraucarpan contains an isopentenyl and two OMe groups, and ring D a methylenedioxy-group as indicated by structure (5). The PMR signals from the



(12) R_1 = Me; R_2 = OMe; R_3 = H
(14); R_1 = H; $R_2 + R_3 = OCH_2O$

isopentenyl-group were similar to those of edudiol (2). The singlet (60 MHz) at τ 4.05 (2H) is characteristic of the methylene dioxy-group, whilst the presence of the two OMe groups is inferred from the singlets at τ 6.12 (3H) and 6.18 (3H). Comparison with published data of 8,9-oxygenated pterocarpans [9] permitted assignment of signals at τ 3.30 and 3.57 to the *para* oriented protons at C-7 and C-10 respectively. The lower τ value of the remaining proton suggests a substitution different from that of compounds (1) and (2). This was supported by colour differences when sprayed with acidic $FeCl_3$.

Similar coloration was observed when neoraucarpanol (9) and ficinin (15) [10] with a pyrogallol oxygenation system, were sprayed with $HClO_4/FeCl_3$.



(15)

Neorautanin (6), $C_{22}H_{22}O_6$ (M^+ 382), gives a red colour with $HClO_4/FeCl_3$. Less information was available on this minor constituent of *N. edulis*, but structure (6) could be established on spectroscopic evidence. The nature of groups present in neorautanin was indicated by PMR. The singlets at τ 4.05 (2H) and 6.03 (3H) are characteristic of a methylenedioxy and OMe group respectively. The singlet at τ 8.63 (6H), the triplets at 8.22 and 7.22 (*J* 7 Hz) are assigned to the protons of the *gem*-CMe_2 group and two methylene-groups of a 2,2-diMechromane moiety [11]. The PMR signals of the aromatic protons at τ 3.75, 3.24 and 3.50 are virtually the same as those for the H-4, H-7 and H-10 signals in the spectra of neoraucarpan (5). The remainder of the PMR spectrum and MS are consistent with the proposed structure.

The IR spectrum of edulenol (7) showed OH absorption but no carbonyl absorption. The MS gave a parent ion at *m/e* 368, which agrees with the empirical formula $C_{22}H_{24}O_5$. The PMR spectrum of (7) in $CDCl_3$ was consistent with the proposed pterocarpanoid structure [4]. In the aromatic region an ABX system was present together with a singlet at τ 3.72 allocated to the 4-H proton. The two 3 proton singlets at τ 6.04 and 6.26 and highfield singlets at τ 8.15 and 8.27 were assigned to O-Me groups and Me groups of the isopentenyl side chain at C-2. The chemical reactions of edulenol confirmed structure (7). Acetylation with Py/Ac_2O produced a monoacetate (8) (M^+ 410) and the C-4 proton was shifted to τ 3.49 ($\Delta\tau$, 0.23) in the PMR spectrum. Acid catalyzed ring closure in dry benzene gave edulane (1) (NMR, MS, IR comparison).

Neoraucarpanol (9), $C_{22}H_{22}O_6$ (M^+ 382), like neoraucarpan (5) gave a brown-yellow colour when sprayed

with $HClO_4/FeCl_3$. The PMR spectrum includes signals singlets from a methylenedioxy group, a 2-proton singlet at τ 4.15 and one OMe group, 3-proton singlet at τ 6.33. The remainder of the spectrum exhibits signals expected for structure (9). Formation of a monoacetate (10) established the presence of a single OH-group (τ 4.50—exchangeable with D_2O).

Large negative optical rotations ($[\alpha]_D$ −258, −248, −298, −303, −253 and −151) were recorded for compounds (1), (2), (5), (6), (7) and (9) respectively, indicating that they possess the 6aR, 11aR absolute configuration common to laevorotatory pterocarpans [12].

From the phytochemical examination of *N. edulis* and *N. amboensis* 11 classes of flavonoid have been identified, viz. flavone [14], isoflavone [15], isoflavanone [15], isoflavan-4-ol [14], isoflavan [2], isoflavene [2], pterocarpan [13], pterocarpen [13], 3-phenylcoumarin [14], 2-phenylbensofuran [2] and rotenoid [1]. With the exception of the 2-phenylbenzofuran all contain a 1,3-diarylpropane unit (C_6–C_3–C_6) which is accommodated in either a 2- or 3-phenylchroman structure. It is conceivable that they arise biosynthetically from the same precursors since it is well known that transformations occur in plants (e.g. isoflavone → rotenoid; chalcone → isoflavone).

EXPERIMENTAL

Mp's were determined with a Kofler hot-stage microscope and are uncorrected. PMR spectra were recorded at 60 MHz with solns in $CDCl_3$ using TMS as internal standard. MS were recorded at 70 eV. Preparative-TLC was carried out on Si gel 60 PF_{254} plates (1 mm thick).

Extraction of root bark of N. edulis. Total root material (900 g), collected at Towoomba Research Station, Transvaal, South Africa, was dried, powdered, and successively extracted with hexane (24 hr), giving fraction A (12.6 g) and Et_2O (24 hr), giving fraction B (9 g). Fraction A (6 g) was chromatographed on Si gel (230–400 mesh) (180 g), using hexane—C_6H_6 (6:4) as eluting solvent giving 5 main fractions (A_1–A_5). A_1 (750 mg) and A_2 (1.03 g) were fatty materials which were not further examined. A_3 (1.68 g) contained known compounds like stigmasterol, (−)-neodunol[13], (−)-neorautenol[13] and (−)-homoedudiol[13]. A_4 (1.32 g) and A_5 (690 mg) were submitted to preparative-TLC. Neoraucarpan (5) was obtained from A_5 after TLC in $CHCl_3$, R_f 0.63 and crystallization from MeOH as short colourless needles (220 mg), mp 140–141°; M^+ 396; $[\alpha]_D^{20}$ −298 (*c* 1.2 in $CHCl_3$); τ ($CDCl_3$) 8.23, *s*, Me_A; 8.34, *s*, Me_B; 6.62, *d*, *J* 7 Hz, $C\underline{H}_{2D}$; 4.82, *br t*, *J* 7 Hz, $=C\underline{H}_C$; 6.53, *m*, 6a-H; 6.43, *m*, 6_{ax}-H; 5.72, *m*, 6_{eq}-H; 6.18, *s*, OMe; 6.12, *s*, OMe; 4.52, *d*, *J* 6.5 Hz, 11a-H; 4.05, *s*, $OC\underline{H}_2O$; 3.53, *s*, 10-H; 3.25, *s*, 7-H; 3.08, *s*, 1-H. Fraction A_4 gave (1) and (6) after TLC in hexane–Me_2CO (9:1). Edulane (1), R_f 0.51, crystallized as colourless needles, mp 174–175° (C_6H_6); M^+ 368; $[\alpha]_D^{20}$ −258 (*c* 0.2 in $CHCl_3$); τ ($CDCl_3$) 8·65, *s*, CMe_2; 8.24, *t*, *J* 6.5 Hz, 3′-CH_2; 7.23, *t*, *J* 6.5 Hz, 4′-CH_2; 6.54, *m*, 6a-H; 6.38, *m*, 6_{ax}-H; 5·83, *m*, 6_{eq}-H; 4.32, *d*, *J* 6.5 Hz, 11a-H; 6.24, *s*, OMe; 6.02, *s*, OMe; 3.75, *s*, 4-H; 3.76, *q*, *J* 9 Hz, *J* 2.5 Hz, 8-H; 3.48, *d*, *J* 2.5 Hz, 10-H; 2.87, *d*, *J* 9 Hz, 7-H. Neorautanin (6), R_f 0.42, M^+ 382, $[\alpha]_D^{21}$ −303 (*c* 0.2 in $CHCl_3$) was obtained as colourless needles, mp 202–204° (C_6H_6–hexane); τ($CDCl_3$) 8.63, *s*, CMe_2; 8.22, *t*, *J* 7 Hz, 3′-CH_2; 7.22, *t*, *J* 7 Hz, 4′-CH_2; 6.55, *m*, 6a-H; 6.37, *m*, 6_{ax}-H; 5.82, *m*, 6_{eq}-H; 4.31, *d*, *J* 6 Hz, 11a-H; 6.03, *s*, OMe; 4.05, *s*, $OC\underline{H}_2O$; 3.73, *s*, 4-H; 3.50, *s*, 10-H; 3.24, *s*, 7-H. Fraction B (5 g) was chromatographed (Si gel, 150 g; hexane–Me_2CO) and the main fraction after preparative-TLC ($CHCl_3$–EtOAc; 13:7) gave edudiol (2) as a brown oil, R_f 0.49, M^+ 354 (M^+ 356; after D_2O addition), $[\alpha]_D^{21}$ −248 (*c* 0.1 in $CHCl_3$).

Extraction of root bark of N. amboensis. Total root bark (450 g). collected near Tsokwane, Kruger National Park, Transvaal, South Africa, was dried, powdered, and extrated with hexane (24 hr) giving a brown syrup (30 g). A 10 g portion was chromatographed on Si gel (230–400 mesh) (400 g), using hexane–C_6H_6–Me_2CO (3:1:1) as eluting solvent. The main fraction (5 g) was rechromatographed with hexane–C_6H_6–Me_2CO (5:4:1). Fractionation of the main fraction by PLC in $CHCl_3$–Et_2O (19:1) gave edulenol (7) (305 mg), R_f 0.6 and neoraucarpanol (9) (150 mg), R_f 0.67. Edulenol (7) was crystallized from C_6H_6 as short colourless needles, mp 118–120°; M^+ 367; $[\alpha]_D$ −253 (*c* 0.3 in $CHCl_3$); τ ($CDCl_3$) 8.27, *s*, Me_A; 8.18, *s*, Me_B; 4.71, *t*, *J* 6.5 Hz, $=CH_C$; 6.61, *d*, *J* 6.5 Hz, CH_{2D}; 6.53, *m*, 6a-H; 6.38, *m*, 6_{ax}-H; 5.84, *m*, 6_{eq}-H; 4.33, *d*, *J* 6.5 Hz, 11a-H; 6.26, *s*, OMe; 6.04, *s*, OMe; 3.72, *s*, 4-H; 3.55, *q*, *J* 9 Hz, *J* 2.5 Hz, 8-H; 3.51, *d*, *J* 2.5 Hz, 10-H; 2.87, *d*, *J* 9 Hz, 7-H; 4.33, O$\underline{H}$. Neoraucarpanol (9) was obtained as a glass, mp 52–54°; M^+ 382; $[\alpha]_D^{18}$ −151 (*c* 0.02 in $CHCl_3$); τ ($CDCl_3$) 8.33, *s*, Me_A; 8.42, *s*, Me_B; 6.70, *d*, *J* 7 Hz, CH_{2D}; 4.86, *t*, *J* 6.5 Hz, $=C\underline{H}_C$; 3.09, *s*, 1-H; 3.39, *s*, 7-H; 3.56, *s*, 10-H; 4.25, *s*, $OC\underline{H}_2O$; 4.50, *br s*, O$\underline{H}$; 4.66, *d*, *J* 6.5 Hz, 11a-H; 5.75, *m*, 6_{eq}-H; 6.33, *s*, OMe; 6.50, *m*, 6_{ax}-H; 6.63, *m*, 6a-H.

2″2″-DiMe-6,7,5″,6″-chromane-5,2′,4′-trimethoxyisoflavone (11). (1) (70 mg) was hydrogenated in EtOAc–HOAc (1:1) (15 ml) containing 10% Pd–C at 50° for 3 hr at 6 atm. After filtration and work-up the phenol was methylated with CH_2N_2 to give (6) as a colourless oil, M^+ 384 (Found: 384.19379. $C_{23}H_{28}O_5$ requires: 384.19366); τ (60 MHz) 8.67, *s*, CMe_2; 8.27, *t*, *J* 6.5 Hz, 3″-CH_2; 7.26, *t*, *J* 6.5 Hz, 4″-CH_2; 5.70, *q*, *J* 10 Hz, *J* 3.5 Hz; 6.02, *t*, *J* 10 Hz, 2-H; 6.21–6.60, *m*, 3-H; 7.04–7.27, *br s*, 4-H; 6.25, *s*, 2-OMe; 6.18, *s*, OMe; 2.93, *d*, *J* 2.8 Hz, 3′-H; 3.48, *q*, *J* 9, 2.8 Hz, 5′-H; 3.53, *d*, *J* 9 Hz, 6′-H; 3.75, *s*, 8-H.

2-Isopentenyl-1,3,9-trimethoxypterocarpan (3). Methylation of (2) (25 mg) with CH_2N_2 gave (3) as a colourless oil after TLC separation in C_6H_6–hexane (3:2), R_f 0.34; M^+ 382; τ ($CDCl_3$) 8.29, *s*, Me_A; 8.20, *s*, Me_B; 6.63, *d*, *J* 7 Hz, CH_{2D}; 4.74, *t*, *J* 7 Hz, $=CH_C$; 6.53, *m*, 6a-H; 6.36, *m*, 6_{ax}-H; 5.79, *m*, 6_{eq}-H; 4.31, *d*, *J* 6.5 Hz, 11a-H; 6.18, *s*, OMe; 6.19, *s*, OMe; 6.01, *s*, OMe; 3.69, *s*, 4-H; 3.58, *d*, *J* 2.5 Hz, 10-H; 3.52, *q*, *J* 8.5, 2.5 Hz, 8-H; 2.82, *d*, *J* 8.5 Hz, 7-H.

2′,2′-DiMe-2,3:5′,6′-chroman-1,9,-dimethoxypterocarpan (1). A mixture of (2) (90 mg), *p*-TsOH (100 mg) and dry C_6H_6 (100 ml) was refluxed in a Dean–Stark apparatus for 45 min. The main fraction, R_f 0.51 in C_6H_6–hexane (4:1) was methylated in Me_2CO with Me_2SO_4–K_2CO_3 to give (1) (23 mg), mp 139°, M^+ 396, identical to the natural product.

2′-Hydroxy-6-isopentyl-7,8-dimethoxy-4′,5′-methylenedioxy isoflavan (13). Hydrogenolysis of (5) (80 mg) according to standard procedures gave (13) (63 mg) as a light brown oil, M^+ 400; τ (60 MHz) 9.06, *s*, Me_A; 9.14, *s*, Me_B; 8.56, *t*, *J* 7.5 Hz, CH_{2C}; 7.50, *t*, *J* 7.5 Hz, CH_{2D}; 7.34, *d*, *J* 7 Hz, 4-CH_2; 6.34–6.54, *m*, 3-H; 5.78, *q*, *J* 10, 3.8 Hz; 6.08, *t*, *J* 10 Hz; 6.23, *s*, OMe; 4.16, *s*, OCH_2O; 3.61, *s*, 3′-H; 6.19, *s*, OMe; 3.40, *s*, 6′-H; 3.24, *s*, 5-H; 6.00, *br s*, OH.

2-Isopentenyl-1,3,9-trimethoxypterocarpan (3). An excess of CH_2N_2–Et_2O was added to a soln of (2) (30 mg) in Et_2O (25 ml) at −5°. The mixture was left for 24 hr at −15°, excess CH_2N_2 removed by dropwise addition of HOAc, and the soln evaporated. (3) (23 mg) was obtained as a pale yellow oil, M^+ 382; τ ($CDCl_3$) 8.31, *s*, Me_A; 8.22, *s*, Me_B; 4.78, *t*, *J* 6.5 Hz, $=CH_C$; 6.65, *d*, *J* 6.5 Hz, CH_{2D}; 6.55, *m*, 6a-H; 6.38, *m*, 6_{ax}-H; 5.83, *m*, 6_{eq}-H; 4.33, *d*, *J* 6.5 Hz, 11a-H; 6.25, *s*, OMe; 6.22, *s*, OMe; 6.04, *s*, OMe; 3.72, *s*, 4-H; 3.58, *q*, *J* 9 Hz, 2.5 Hz, 8-H; 3.50, *d*, *J* 2.5 Hz, 10-H; 2.89, *d*, *J* 9 Hz, 7-H.

3-Acetoxy-2-isopentenyl-1,9-dimethoxypterocarpan (4). Acetylation of (2) (30 mg) with Ac_2O (0.5 ml) in Py (1 ml) gave (4) (25 mg) as fine white needles (C_6H_6–hexane), mp 162–164°; M^+ 410; τ ($CDCl_3$) 8.30, *s*, Me_A; 8.23, *s*, Me_B; 7.75, *s*, OCOMe; 4.85, *t*, *J* 6.5 Hz, =CH; 6.70, *d*, *J* 6.5 Hz, CH_{2D}; 6.53, *m*, 6a-H; 6.38, *m*, 6_{ax}-H; 5.78, *m*, 6_{eq}-H; 4.33, *d*, *J* 6.5 Hz, 11a-H; 6.23, *s*, OMe; 6.03, *s*, OMe; 3.55, *q*, *J* 9, 2.5 Hz, 8-H; 3.52, *d*, *J* 2.5 Hz, 10-H; 2.87, *d*, *J* 9 Hz, 7-H; 3.49, *s*, 4-H.

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