product was extracted twice with an equal vol. of C_6H_6 and dried over anhydrous Na_2SO_4. GLC analysis (OV-101, 100°, isothermal program) indicated 95% purity. The MS *m/e* 138 (M^+) and UV spectrum λ_{max} 368 nm [14] were consistent with MQ.

Enzymatic reaction. Reaction mixtures (50 ml) contained 10mM sodium phosphate, pH 6.5, 10 mM H_2O_2 and various concs of phenolic substrates as indicated. Reactions were started by the addition of 50 µl peroxidase (50 µg) and were carried out at 38°. At the end of the incubation, 2 ml 2 N H_2SO_4 were added and the mixture was immediately extracted with EtOAc (2 × 30 ml). The combined organic fractions were dried and evapd to dryness in N_2. Trimethylsilanation of enzymatic products and standards was carried out by adding *bis*-(*N,O*-trimethylsilyl)trifluoroacetamide–pyridine (1:1) to the dry residue and heating at 80° for 5 min.

Gas chromatography. GLC was carried out with a Varian Model 1700 instrument fitted with a glass column (180 × 0.2 cm i.d.) packed with 3% OV-101 on chromosorb Q 100/120 (Applied Science). The oven temp. was programmed from 100 to 270° at 10°/min unless indicated otherwise. MS was carried out with a Dupont Model 21-491B equipped with the same instrument and column for GLC. The spectra were obtained at 70 eV.

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OVALIN, A NEW PIPECOLIC ACID FROM *MILLETIA OVALIFOLIA* SEEDS

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Key Word Index—*Milletia ovalifolia*; Leguminosae; ovalin.

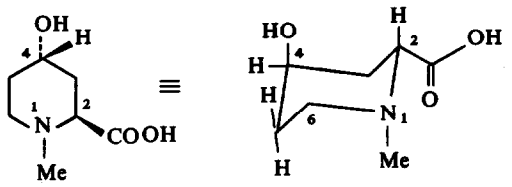
In continuation of our earlier work [1], further examination of *Milletia ovalifolia* seeds led to the isolation of a new pipecolic acid, ovalin, from the methanol extract. Ovalin was obtained chromatographically pure as colourless needles from EtOH–Me_2CO; mp 280–281° (decomp.); R_f 0.36 (PC *n*-BuOH–HCO_2H–H_2O, 15:3:2). It analysed for $C_7H_{13}NO_3$; M^+ 159; $[\alpha]_D^{20}$ −41.2° (H_2O) was chemically neutral and insoluble in all organic solvents except alcohol in which it was partially soluble, but was readily soluble in H_2O. There was no UV absorption in the range 200–300 nm. The IR spectrum (KBr) indicated an —OH group (ν 3350 cm^{-1}), $\rangle$=O of carboxylate (1630 cm^{-1}) and a quaternary ammonium group (=N^+=) (1400 cm^{-1}). It did not respond to tests for amino acids, peptides and alkaloids. The inertness towards most of the reagents and the presence of nitrogen suggested it to be a pipecolic acid derivative, some of which are known to occur in the seeds of leguminous plants [2].

The ^1H NMR spectrum (60 MHz, solvent D_2O, values) indicated the presence of $\rangle$N—Me group, methine and methylene protons. The spectrum closely resembled that of 4-hydroxypipecolic acid recorded in D_2O [3–5]. A quintet centred at 4.3 ($J_{ae} = J_{ee} = 3.5$ Hz, 1H) was assigned to an equatorial C-4 proton. A pair of doublets centred at 3.85 ($J_{ae} = 5$; $J_{aa} = 11$ Hz, 1H) was assigned to an axial C-2 proton because of the large coupling constant, characteristic of axial–axial neigh-

bours. The C-6 protons and four methylene protons appeared as multiplets at 3.2–3.6 (2H) and 1.9–2.4 (4H), respectively. A singlet at 3.0 (3H) was attributed to the =N—Me protons.

Ovalin formed a methyl ester with ethereal CH_2N_2 as a gummy mass, R_f 0.58 (PC *n*-BuOH–HCO_2H–H_2O, 15:3:2); IR (KBr) cm^{-1}: 3400 (OH) and 1730 (C=O of ester). ^1H NMR (60 MHz, solvent D_2O): δ 4.1–4.6 (2H, *m*), 3.55–3.85 (2H, *m*), 3.35 (3H, *s*), 3.3 (3H, *s*) and 2.0–2.5 (4H, *br m*). On acetylation with Ac_2O–$HClO_4$, ovalin formed a monoacetate as an oil; R_f 0.57 (PC *n*-BuOH–HCO_2H–H_2O; 15:3:2). IR (Nujol) cm^{-1}: 1750 and NMR (solvent D_2O); δ 4.2 (2H, *br m*), 3.5 (2H, *m*), 3.0 (3H, *s*, =N—Me), 2.3 (3H, *s*, —OAc) and 1.9–2.3 (4H, *m*). Formation of a monoacetate and methyl ester supported the presence of a hydroxyl and carboxyl group. Based on the above data, structure (1) is proposed for ovalin which is supported by MS fragmentations *m/e* 114 (99.5) ($M^+ - 45$), 96 (100) ($M^+ - 45 - 18$) and 70 (99.9%).

Ovalin showed a positive Cotton effect at 205 nm ($\Delta\varepsilon$ +0.00453) in the circular dichroism spectrum recorded in H_2O similar to (−)-*trans*-4-hydroxypipecolic acid which has a positive Cotton effect at 204 nm ($\Delta\varepsilon$ +0.0061) in H_2O [6]. The above data suggest that ovalin is (2*S*,4*R*)-4-hydroxy-*N*-methylpipecolic acid.



1

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N-METHYLTYRAMINE, A BIOLOGICALLY ACTIVE AMINE IN *ACACIA* SEEDS

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Key Word Index—*Acacia*; Leguminosae; chemotaxonomy; *N*-methyltyramine; migraine.

Abstract—The seeds of *Acacia* species belonging to the 'pennata' group characteristically contain *N*-methyltyramine (approximately 0.5% dry weight). Like tyramine, *N*-methyltyramine increases blood pressure in the anaesthetized rat, relaxes guinea pig ileum and increases both the force and rate of contraction of guinea-pig right atrium by inducing the release of noradrenaline.

INTRODUCTION

Seven *Acacia* species, *A. bonariensis* Gill. ex Hook & Arn., *A. brevispica* Harms., *A. caesia* W. & A., *A. kraussiana* Meisn. ex Benth., *A. schweinfurthii* Brenan & Exell, *A. pennata* (L.) Willd., *A. pentagona* (Schumach & Thonn.) Hook f., belonging to the 'pennata' group of Bentham's series Vulgares were reported recently to accumulate an unidentified ninhydrin-reacting compound in their seeds [1]. We have now isolated this compound from seeds of *A. schweinfurthii* Brenan & Exell, and identified it as *N*-methyltyramine (NMT).

This is, as far as we are aware, the first report of NMT in *Acacia* seeds but it is known to occur in leaves of *A. rigidula*, *A. roemeriana* and *A. berlandieri* [2, 3]. The leaves of *A. berlandieri* (Guajillo) also contain tyramine, and when eaten by sheep and goats in the Pecos region of Texas they cause a neurological disease known as 'guajillo wobbles' or 'limerleg' which affects the animal's gait [3].

While isolating NMT from *A. schweinfurthii*, one of us (C.S.E.) developed acute migraine-type headaches, which