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# 7,8,4′-TRIHYDROXY-3,3′-DIMETHOXYFLAVONE FROM THE HEARTWOOD OF *ACACIA NIGRESCENS*

ELFRANCO MALAN

Department of Chemistry, University of Durban-Westville, Private Bag X54001, Durban, 4000, South Africa

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**Key Word Index**—*Acacia nigrescens*; Leguminosae; heartwood; 7,8,3′,4′-tetrahydroxy-3-methoxyflavone; 7,8,4′-trihydroxy-3,3′-dimethoxyflavone; 7,8,4′-trihydroxyflavanone.

**Abstract**—Two partially methylated flavonols 7,8,3′,4′-tetrahydroxy-3-methoxyflavone, and 7,8,4′-trihydroxy-3,3′-dimethoxyflavone were isolated together with 7,8,4′-trihydroxyflavone from the heartwood of *Acacia nigrescens*.

## INTRODUCTION

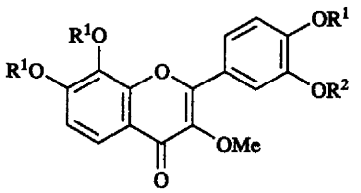
During an endeavour to isolate some of the known metabolites [1] from the heartwood of *Acacia nigrescens* as material for a future synthesis, two partially *O*-methylated derivatives of 3,7,8,3′,4′-pentahydroxyflavone (melanoxetin) [2, 3] were isolated. The rare 7,8,4′-trihydroxyflavanone [4] was also found amongst a series of flavonoids with an exclusively based 7,8,3′,4′-tetrahydroxyl pattern [1].

## RESULTS AND DISCUSSION

Countercurrent and column chromatography separations of the acetone extract of the heartwood of *Acacia nigrescens* resulted in the isolation of 7,8,3′,4′-tetrahydroxy-3-methoxyflavone (**1a**), previously found in *Artemisia transiliensis* [5], *A. cyperophylla* and *A. sowdenii* [6], the newly discovered 7,8,4′-trihydroxy 3,3′-dimethoxyflavone (**2a**) and 7,8,4′-trihydroxyflavone.

The $^1$H NMR spectra of the two partially *O*-methylated flavonols (**1a**, **2a**) showed a typical *ortho*-coupled pattern for H-5 and H-8 of the A-ring and an ABX system for the H-2′, H-5′ and H-6′ protons of the B-ring (Table 1). The position of the methoxy groups was determined by NOE experiments which confirmed an association of the 3-*O*-methyl group of **1a** and **2a** with both H-2′ (2.8; 2.1%) and H-6′ (2.2; 2.1%) the 3′-methoxy of **2a** showed an association of 2.4% with H-2′. Acetylation ($Ac_2O$–pyridine) of **1a** and **2a** resulted in the tetra- and triacetates (**1b**, **2b**), respectively (Table 1).

Mass spectral analysis confirmed the structures of **1a** and **1b** with molecular ions at 316 (100%) and 484 (17%), while **2a** and **2b** have molecular ions at 330 (100%) and 456 (11%), respectively. The A-ring pattern for both **1a** and **2a** was confirmed by fragments *m/z* 152 and 153. Confirmation of the B-ring substitution was shown by *m/z* 137 (14%) for **1a** and *m/z* 151 (10%) for **2a**.




| | $R^1$ | $R^2$ |
|---|---|---|
| **1a** | H | H |
| **1b** | Ac | Ac |
| **2a** | H | Me |
| **2b** | Ac | Me |

## EXPERIMENTAL

*Plant material. Acacia nigrescens* was collected and identified by Mrs L. Davies of the National Parks Board at Skukuza, Eastern Transvaal.

*Extraction and isolation.* The milled heartwood of *A. nigrescens* was defatted with hexane followed by extraction with $Me_2CO$ at 30°. After sepn by countercurrent and CC (Merck 7734, $C_6H_6$–$Me_2CO$, 2:1) techniques the isolated compounds were present in the bands with $R_f$ 0.16 (**1a**) and $R_f$ 0.23 (**2a**) when analysed on Merck TLC 5554 in $C_6H_6$–$Me_2CO$, 4:3.

7,8,3′,4′-*Tetrahydroxy*-3-*methoxyflavone* (**1a**). Noncrystalline, 12 mg. UV $\lambda_{max}^{MeOH}$ nm: 254, 276, 320, 365, 380 (log ε 3.67, 3.64, 3.46, 3.43, 3.47). MS: $[M]^+$ *m/z* 316.0582, $C_{16}H_{12}O_7$ requires: 316.0581, *m/z* (rel. int.) 316 (100), 273 (20), 153 (44), 152 (26), 137 (14). Acetate (**1b**). Noncrystalline. ($R_f$ 0.23, $C_6H_6$–$Me_2CO$, 9:1). IR $\nu_{max}^{CHCl_3}$ cm$^{-1}$: 1498, 1613, 1644, 1773. MS: *m/z* (rel. int.): 484 (17), 442 (33), 400 (73), 358 (100), 316 (81).

7,8,4′-*Trihydroxy*-3,3′-*dimethoxyflavone* (**2a**). Noncrystalline, 16 mg. UV $\lambda_{max}^{MeOH}$ nm: 250, 314, 350 (log ε 3.89, 3.66, 3.77). MS $[M]^+$ 330.0733 $C_{17}H_{14}O_7$ requires:

Table 1. $^1$H NMR spectral data (300 MHz) of *Acacia* flavonols

| H | **1a** ($CDCl_3$) | **1b** (acetone-$d_6$) | **2a** ($CDCl_3$) | **2b** (acetone-$d_6$) |
|---|---|---|---|---|
| 5 | 8.13 *d* | 7.54 *d* | 7.97 *d* | 7.73 *d* |
| 6 | 7.22 *d* | 6.96 *d* | 7.09 *d* | 6.99 *d* |
| 2′ | 7.84 *d* | 7.73 *d* | 8.02 *d* | 7.75 *d* |
| 5′ | 7.32 *d* | 6.98 *d* | 7.34 *d* | 7.0 *d* |
| 6′ | 7.88 *d* | 7.63 *dd* | 8.05 *dd* | 7.63 *dd* |
| OMe | 3.85 *s* (3H) | 3.83 *s* (3H) | 3.90–4.0 *s* (6H) | 3.85–4.01 *d* (6H) |
| OAc | 2.32–2.40 *t* (12H) | | 2.32–2.38 *t* (9H) | |

330.0735, *m/z* (rel. int.): 330 (100), 287 (14), 153 (10), 152 (12), 151 (10). Acetate (**2b**). Non-crystalline. ($R_f$ 0.28, $C_6H_6$–$Me_2CO$, 9:1). IR $\nu_{max}^{CHCl_3}$ cm $^{-1}$: 1498, 1613, 1636, 1766. MS: *m/z* (rel. int.): 456 (11), 414 (23), 372 (49), 330 (100).

(±)-7,8,4′-*Triacetoxyflavanone*. Non-crystalline, 3 mg. ($R_f$ 0.31, $C_6H_6$–$Me_2CO$, 9:1) $^1$H NMR; 7.84 (1H, *d*, H-5), 7.43 (2H, *d*, H-2′ and H-6′), 7.13 (2H, *d*, H-3′ and H-5′), 6.89 (1H, *d*, H-6), 5.50 (1H, *q*, H-2), 3.04 (1H, *q*, H-3 ax), 2.88 (1H, *q*, H-3 eq), 2.31 (2) and 2.25 for 3 × OMe. MS: $[M]^+$ *m/z* 398 (16%).

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