

LIMONIDS FROM LEAVES OF *KHAYA SENEGALENSIS*\*LIS R. V. OLMO, M. FÁTIMA DAS G. F. DA SILVA,† EDSON RODRIGUES FO., PAULO C. VIEIRA,  
JOÃO B. FERNANDES, ANTÔNIO L. PINHEIRO‡ and EVALDO F. VILELA§

Departamento de Química, Universidade Federal de São Carlos, Caixa Postal 676, 13565-905 São Carlos, SP, Brazil;

‡ Departamento de Engenharia Florestal, Universidade Federal de Viçosa, 36570-000 Viçosa, MG, Brazil; § Departamento de Biologia Animal, Universidade Federal de Viçosa, 36570-000 Viçosa, MG, Brazil

(Received in revised form 8 July 1996)

**Key Word Index**—*Khaya senegalensis*; Meliaceae; limonoids; coumarins; flavonoids; biochemical systematics.**Abstract**—The leaves of *Khaya senegalensis* yielded two new limonoids. These compounds were identified on the basis of spectroscopic analysis as methyl 1 $\alpha$ -acetoxy-3 $\beta$ ,6,8 $\alpha$ -trihydroxy-2 $\alpha$ -methoxy-2 $\beta$ ,14 $\beta$ -epoxy-[4.2.1<sup>10,30</sup>.1<sup>1,4</sup>]-tricyclomeliac-7-oate and methyl 1 $\alpha$ -acetoxy-6,8 $\alpha$ ,14 $\beta$ ,30 $\beta$ -tetrahydroxy-3-oxo [3.3.1<sup>10,2</sup>.1<sup>1,4</sup>]-tricyclomeliac-7-oate. Scopoletin,  $\beta$ -quercitrin and rutin were also isolated. Copyright © 1997 Elsevier Science Ltd

## INTRODUCTION

Recently, we have described the isolation and identification of three limonoids, methyl 1 $\alpha$ ,6,8 $\alpha$ ,14 $\beta$ ,30 $\beta$ -pentahydroxy-3-oxo[3.3.1<sup>10,2</sup>.1<sup>1,4</sup>]-tricyclomeliac-7-oate; methyl 1 $\alpha$ ,2 $\beta$ ,3 $\alpha$ ,6,8 $\alpha$ ,14 $\beta$ -hexahydroxy-[4.2.1<sup>10,30</sup>.1<sup>1,4</sup>]-tricyclomeliac-7-oate and methyl 1 $\alpha$ -acetoxy-2 $\beta$ ,3 $\alpha$ ,6,8 $\alpha$ ,14 $\beta$ -pentahydroxy-[4.2.1<sup>10,30</sup>.1<sup>1,4</sup>]-tricyclomeliac-7-oate from the stem of *Khaya senegalensis* [1]. The last two compounds represent a novel group of methyl tricyclomeliac-7-oates.

The isolation of this interesting group of new compounds, combined with our taxonomic interest in the Meliaceae, stimulated an investigation of the leaves of *K. senegalensis*. Two new limonoids (**1**, **2**) have now been isolated along with the known scopoletin,  $\beta$ -quercitrin and rutin [2–4].

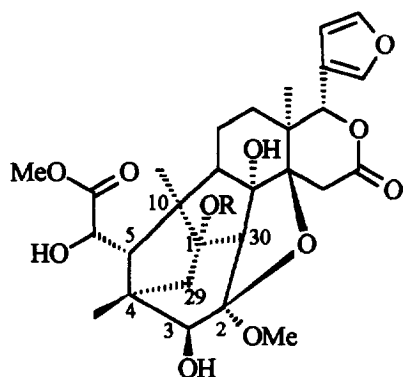
## RESULTS AND DISCUSSION

The limonoid **1** showed spectral characteristics (Tables 1 and 2) close to those of methyl 1 $\alpha$ -acetoxy-2 $\beta$ ,3 $\alpha$ ,6,8 $\alpha$ -14 $\beta$ -pentahydroxy-[4.2.1<sup>10,30</sup>.1<sup>1,4</sup>]-tricyclomeliac-7-oate (**3**) [1]. The principal change observed in the <sup>13</sup>C NMR spectrum (Table 2) of compound **1** was the replacement of the resonance for an oxymethine by a signal of a ketal (or hemiketal) carbon ( $\delta$  104.9). The <sup>1</sup>H (Table 1) and <sup>13</sup>C NMR showed the

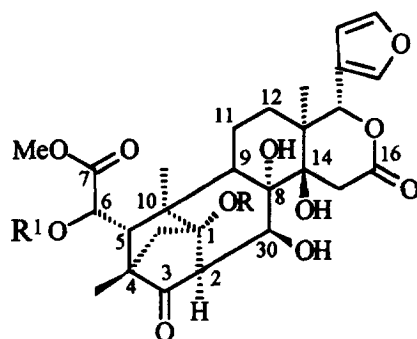
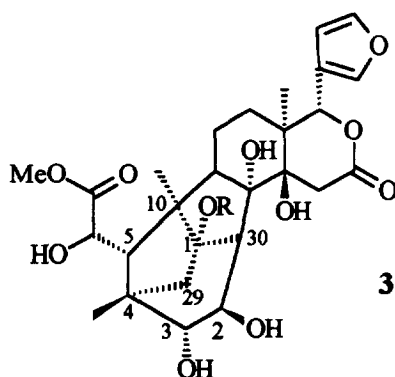
existence of two methoxyl groups ( $\delta_C$  52.6 and 50.4;  $\delta_H$  3.78 s and 3.33 s). The signal for H-3 at  $\delta$  3.48 showed one-bond correlation (HMQC) with the <sup>13</sup>C signal at  $\delta$  82.4 and was coupled only to the <sup>1</sup>H signal of a hydroxyl group ( $\delta$  2.86, D<sub>2</sub>O exch.). In the same way, the signal for H-30 was visible as a singlet at  $\delta$  3.29 and showed cross peaks with the <sup>13</sup>C signal at  $\delta$  68.8 (<sup>1</sup>J). Thus, the deshielded resonances observed here, when compared with compound **3**, required the presence of an acyclic hemiketal involving a tertiary hydroxyl and methoxyl functions at C-2 or a cyclic ketal formed by joining C-2 to O-14 and methoxyl group at C-2. The cyclic nature of the ketal function was apparent from the significant downfield shifts for C-14 (**1**:  $\delta$  83.4; **3**:  $\delta$  81.5) and C-15 (**1**:  $\delta$  35.8; **3**:  $\delta$  32.0) in the <sup>13</sup>C NMR spectrum, when compared with **3**. The correct one was also decided on the basis of the <sup>13</sup>C NMR spectrum, by means of isotope shifts [5] observed in the H<sub>2</sub>O/D<sub>2</sub>O experiment, which did not show any significant effect at C-2. Compound **1** failed to give an [M]<sup>+</sup>, in the EI-mass spectrum, the largest fragment observed being  $m/z$  447 for [M – (Me, OMe, FuCHO, H)]<sup>+</sup>. However, its PIDCI mass spectrum showed ions at  $m/z$  605 [M + CH<sub>3</sub>]<sup>+</sup>, 591 [M + H]<sup>+</sup>, 573 [M + CH<sub>3</sub> – CH<sub>3</sub>OH]<sup>+</sup>, 559 [M + H – CH<sub>3</sub>OH]<sup>+</sup>, confirming the ketal function and thus the molecular formula (C<sub>30</sub>H<sub>38</sub>O<sub>12</sub>). This was supported by the HMBC (Table 3) spectrum which showed correlations from H-3, H-30 (<sup>2</sup>J) and -OMe ( $\delta$  3.33, <sup>3</sup>J) to the C-2 signal at  $\delta$  104.9. The NOESY (Table 4) experiments showed correlations of H-3 with H<sub>3</sub>-28 and H-29b, and of 3-OH with H-5, requiring H-3 on the  $\alpha$ -side and 3-OH on the  $\beta$ -side of the molecule. The cor-

\* Based in part on the Ph.D. thesis presented by L.R.V.O. to PPGQ-UFSCar.

† Author to whom correspondence should be addressed.



1: R = Ac

2: R = Ac, R<sup>1</sup> = H4: R = R<sup>1</sup> = H4a: R = R<sup>1</sup> = Ac

3: R = Ac

relations from 2-OMe to the signals of H-30 and H-3 showed that the methoxyl group was thus in the  $\alpha$ -configuration. Moreover, the observed correlation of 2-OMe with H-15 $\beta$  implied that they were close to each other in space and suggested that the 2-OMe, together with the cyclic ketal function, may have caused a downfield shift for H-15 $\beta$  (1:  $\delta$  3.50; 3:  $\delta$  2.69). The new natural product was therefore identified as methyl 1 $\alpha$ -acetoxy-3 $\beta$ ,6,8 $\alpha$ -trihydroxy-2 $\alpha$ -methoxy-2 $\beta$ ,14 $\beta$ -epoxy-[4.2.1<sup>10,30,1,4</sup>]-tricyclomeliac-7-oate (1).

The limonoid 2, exhibited similar NMR spectra (Tables 1 and 2) to methyl 1 $\alpha$ ,6,8 $\alpha$ ,14 $\beta$ ,30 $\beta$ -pentahydroxy-3-oxo-[3.3.1<sup>10,2,1,4</sup>]-tricyclomeliac-7-oate (4) [1], except for the presence of a tertiary acetoxy ( $\delta_C$  170.2, 22.0;  $\delta_H$  2.02 s). Significant upfield shifts for C-2 and C-29 in the <sup>13</sup>C NMR spectrum, when compared with 4 and its 1 $\alpha$ ,6-diacetoxy derivative 4a [1], determined the position of the acetoxy at C-1. Thus, the structure of the new limonoid was characterized as methyl 1 $\alpha$ -acetoxy-6,8 $\alpha$ ,14 $\beta$ ,30 $\beta$ -tetrahydroxy-3-oxo-[3.3.1<sup>10,2,1,4</sup>]-tricyclomeliac-7-oate (2).

In biogenetic terms, a pinacol pinacolone rearrangement of a 2,3,30-trihydroxy-1,29-cyclo-

meliacate precursor may have occurred, resulting in a 2-oxo-tricyclo-[4.2.1<sup>10,30,1,4</sup>]-decane. Subsequent reduction or addition of an hydroxyl group at C-14 to ketone and *O*-2-methylation may have led to the limonoids 3 and 1, respectively.

#### EXPERIMENTAL

**General.** NMR: Bruker ARX 400 with TMS as int. standard; EI-MS: 70 eV, direct probe insert and elevated temp, low resolution on a HP-5988 instrument; PIDCI-MS (isobutane): 70 eV, low resolution on a VG Platform II (Fisons) instrument.

**Plant material.** *Khaya senegalensis* was collected in Viçosa, MG, Brazil, and a voucher is deposited in the Herbarium of Departamento de Engenharia Florestal, Universidade Federal de Viçosa, Viçosa, MG.

**Isolation of compounds.** Ground leaves (2000 g) were extracted with hexane, then CH<sub>2</sub>Cl<sub>2</sub> and finally with MeOH. The concd MeOH extract was partitioned into CH<sub>2</sub>Cl<sub>2</sub>-, EtOAc- and *n*-BuOH-soluble frs. The concd CH<sub>2</sub>Cl<sub>2</sub> extract was subjected to CC over silica gel. Elution with a CH<sub>2</sub>Cl<sub>2</sub>-EtOAc-MeOH gradient

Table 1.  $^1\text{H}$  NMR chemical shifts for compounds **1**, **2** and the model compounds **3**, **4** and **4a**

| H           | 1                              | 2                              | 3                              | 4                              | 4a                         |
|-------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|----------------------------|
| 2           |                                | 3.27 <i>d</i><br>(10.4)        | 4.45 <i>dd</i><br>(6.7, 9.5)   | 2.88 <i>d</i><br>(10.3)        | 3.36 <i>d</i><br>(10.4)    |
| 3           | 3.49 <i>d</i> *<br>(9.6)       |                                | 3.42 <i>br d</i><br>(6.7)      |                                |                            |
| 5           | 2.57 <i>d</i><br>(5.6)         | 3.07 <i>d</i><br>(8.4)         | 2.93 <i>d</i><br>(7.0)         | 3.25 <i>d</i><br>(8.0)         | 3.21 <i>d</i><br>(3.6)     |
| 6           | 4.27 <i>dd</i> *<br>(7.2, 5.6) | 4.13 <i>dd</i> *<br>(8.4, 5.0) | 4.15 <i>dd</i> *<br>(7.0, 5.2) | 4.22 <i>dd</i> *<br>(8.0, 5.0) | 5.13 <i>d</i><br>(3.6)     |
| 9           | 2.17 <i>br d</i><br>(8.8)      | 2.30 <i>br d</i><br>(8.4)      | 2.16 <i>br d</i><br>(7.0)      | 2.28 <i>br d</i><br>(10.0)     | 2.31 <i>br d</i><br>(9.6)  |
| 11 $\beta$  | 1.86 <i>m</i>                  | 1.90 <i>m</i>                  |                                | 1.90 <i>m</i>                  | 1.37 <i>m</i>              |
| 11 $\alpha$ | 1.58 <i>m</i>                  | 1.64–1.72 <i>m</i>             |                                | 1.77–1.83 <i>m</i>             | 1.95 <i>m</i>              |
| 12 $\beta$  | 1.80 <i>m</i>                  | 1.64–1.72 <i>m</i>             |                                | 1.77–1.83 <i>m</i>             | 1.66 <i>m</i>              |
| 12 $\alpha$ | 1.07 <i>m</i>                  | 0.74 <i>br d</i><br>(10.8)     | 0.81 <i>m</i>                  | 0.85 <i>br d</i><br>(9.0)      | 0.95 <i>br d</i><br>(10.8) |
| 15 $\beta$  | 3.50<br>(AB, 18.4)             | 2.72<br>(AB, 18.8)             | 2.69<br>(AB, 18.7)             | 2.69<br>(AB, 18.6)             | 2.66<br>(AB, 18.8)         |
| 15 $\alpha$ | 3.08                           | 2.96                           | 3.04                           | 3.10                           | 3.13                       |
| 17          | 5.57 <i>s</i>                  | 5.26 <i>s</i>                  | 5.50 <i>s</i>                  | 5.40 <i>s</i>                  | 5.51 <i>s</i>              |
| 18          | 1.07 <i>s</i>                  | 1.03 <i>s</i>                  | 1.05 <i>s</i>                  | 1.11 <i>s</i>                  | 1.08 <i>s</i>              |
| 19          | 1.29 <i>s</i>                  | 1.33 <i>s</i>                  | 1.21 <i>s</i>                  | 1.33 <i>s</i>                  | 1.44 <i>s</i>              |
| 21          | 7.42 <i>m</i>                  | 7.68 <i>m</i>                  | 7.33 <i>m</i>                  | 7.59 <i>m</i>                  | 7.40 <i>m</i>              |
| 22          | 6.41 <i>m</i>                  | 6.47 <i>m</i>                  | 6.33 <i>m</i>                  | 6.47 <i>m</i>                  | 6.36 <i>m</i>              |
| 23          | 7.47 <i>m</i>                  | 7.67 <i>m</i>                  | 7.37 <i>m</i>                  | 7.56 <i>m</i>                  | 7.30 <i>m</i>              |
| 28          | 1.20 <i>s</i>                  | 0.92 <i>s</i>                  | 1.03 <i>s</i>                  | 0.99 <i>s</i>                  | 1.10 <i>s</i>              |
| 29a         | 1.88<br>(AB, 12.4)             | 2.04<br>(AB, 10.0)             | 1.74<br>(AB, 12.2)             | 1.78<br>(AB, 12.6)             | 2.09<br>(AB, 12.8)         |
| 29b         | 2.53                           | 2.55                           | 2.23                           | 2.11                           | 2.86                       |
| 30          | 3.29 <i>s</i>                  | 4.40 <i>d</i><br>(10.4)        | 3.15 <i>d</i><br>(9.5)         | 4.37 <i>d</i><br>(10.3)        | 4.42 <i>s</i><br>(10.4)    |
| OMe (C-7)   | 3.78 <i>s</i>                  | 3.61 <i>s</i>                  | 3.69 <i>s</i>                  | 3.66 <i>s</i>                  | 3.71 <i>s</i>              |
| OMe (C-2)   | 3.33 <i>s</i>                  |                                |                                |                                |                            |
| OH          | 2.86 <i>d</i> *<br>(9.6)       |                                |                                |                                |                            |
| OH          | 2.54 <i>d</i> *<br>(7.2)       | 6.10 <i>d</i> *<br>(5.0)       | 3.62 <i>d</i> *<br>(5.2)       | 5.44 <i>d</i> *<br>(5.0)       |                            |
| OH          |                                |                                | 5.24 <i>br s</i>               | 4.97 <i>br s</i>               |                            |
| OH          |                                |                                | 4.88 <i>br s</i>               | 4.60 <i>br s</i>               |                            |
| OCOMe       | 2.04 <i>s</i>                  | 2.02 <i>s</i>                  | 1.97 <i>s</i>                  |                                | 2.17 <i>s</i>              |
| OCOMe       |                                |                                |                                |                                | 2.10 <i>s</i>              |

Resonances for compounds **1**, **2**, **4** and **4a** were confirmed by  $^1\text{H}/^1\text{H}$  and  $^{13}\text{C}/^1\text{H}$  shift-correlated two-dimensional spectra. Coupling constants (Hz) in parentheses.

\* Exchangeable with  $\text{D}_2\text{O}$ .

Table 2.  $^{13}\text{C}$  NMR chemical shift for compounds **1**, **2** and the model compounds **3**, **4**, and **4a**

| C         | 1     | 2     | 3     | 4     | 4a    |
|-----------|-------|-------|-------|-------|-------|
| 1         | 91.4  | 90.1  | 91.1  | 83.6  | 91.2  |
| 2         | 104.9 | 58.1  | 72.0  | 62.7  | 59.6  |
| 3         | 82.4  | 205.4 | 78.1  | 206.5 | 204.0 |
| 4         | 44.2  | 50.5  | 44.1  | 49.3  | 52.1  |
| 5         | 39.3  | 40.0  | 39.1  | 41.9  | 40.7  |
| 6         | 72.1  | 69.6  | 71.5  | 70.0  | 72.7  |
| 7         | 175.3 | 173.4 | 175.1 | 173.6 | 170.1 |
| 8         | 86.8  | 86.6  | 86.8  | 86.8  | 87.6  |
| 9         | 56.9  | 54.5  | 55.9  | 54.6  | 57.3  |
| 10        | 61.8  | 60.9  | 60.9  | 59.3  | 62.0  |
| 11        | 16.3  | 16.1  | 16.4  | 16.2  | 16.5  |
| 12        | 26.5  | 26.4  | 26.0  | 26.3  | 25.6  |
| 13        | 37.6  | 37.0  | 37.5  | 36.9  | 37.5  |
| 14        | 83.4  | 83.4  | 81.5  | 83.0  | 83.5  |
| 15        | 35.8  | 33.0  | 32.0  | 33.1  | 32.4  |
| 16        | 170.7 | 169.7 | 170.3 | 169.9 | 169.7 |
| 17        | 80.6  | 80.0  | 80.5  | 80.2  | 79.9  |
| 18        | 15.3  | 14.7  | 14.4  | 14.6  | 14.2  |
| 19        | 18.7  | 18.0  | 18.1  | 18.3  | 20.5  |
| 20        | 120.7 | 120.7 | 120.6 | 120.7 | 120.4 |
| 21        | 143.0 | 141.7 | 142.6 | 141.5 | 141.1 |
| 22        | 110.1 | 110.5 | 110.1 | 110.4 | 110.1 |
| 23        | 141.0 | 143.5 | 140.9 | 143.3 | 143.0 |
| 28        | 19.8  | 15.1  | 19.3  | 15.3  | 15.6  |
| 29        | 40.0  | 40.7  | 41.1  | 44.3  | 40.8  |
| 30        | 68.8  | 74.1  | 58.7  | 74.5  | 74.0  |
| OMe (C-7) | 52.6  | 51.8  | 52.2  | 51.6  | 52.4  |
| OMe (C-2) | 50.4  |       |       |       |       |
| OCOMe     | 170.1 | 170.2 | 170.4 |       | 169.4 |
| OCOMe     |       |       |       |       | 169.3 |
| OCOMe     | 21.9  | 22.0  | 22.0  |       | 21.9  |
| OCOMe     |       |       |       |       | 21.0  |

Assignments based on HMQC/HMBC for **1** and **4a**. HMQC for **2** and  $^1\text{H}$ - $^{13}\text{C}$  COSY/ $^1\text{H}$ - $^{13}\text{C}$  LRCOSY for **4**.

Table 3. HMBC for compound **1**

| H     | C                  |
|-------|--------------------|
| 3     | 2                  |
| 5     | 1, 3, 4, 6, 9, 10  |
| 6     | 10, 7              |
| 9     | 5, 8, 10           |
| 15    | 13, 14, 16         |
| 17    | 18, 20, 21, 22     |
| 18    | 12, 13, 14, 17     |
| 19    | 1, 5, 9, 10        |
| 21    | 20, 22, 23         |
| 22    | 20, 21, 23         |
| 23    | 20, 21             |
| 28    | 3, 4, 5            |
| 29    | 1, 3, 4, 5, 10, 30 |
| 30    | 1, 2, 8, 10        |
| 2-OMe | 2                  |
| 7-OMe | 7                  |

Table 4. NOESY two-dimensional NMR for compound **1**

| H           | H                 |
|-------------|-------------------|
| 3           | 28, 29b, 2-OMe    |
| 5           | 12 $\beta$ , 3-OH |
| 6           | 5, 19, 28         |
| 9           | 8-OH, 11, 19      |
| 15 $\alpha$ | 18                |
| 15 $\beta$  | 30, 2-OMe         |
| 29a         | 19, 28            |
| 30          | 2-OMe, 8-OH, 29b  |
| 6-OH        | 19, 28            |

yielded 22 frs. Frs 1–4 were purified by prep. TLC (silica gel, hexane- $\text{CH}_2\text{Cl}_2$ -MeOH, 25:25:2) to yield scopoletin (4 mg). Frs 5–7 were rechromatographed over silica gel using  $\text{CH}_2\text{Cl}_2$ -MeOH (98:2) and then recrystallized in  $\text{CHCl}_3$ -MeOH, yielding compound **1** (30 mg). Frs 14–16 after CC over silica gel eluting with hexane- $\text{CHCl}_3$ -MeOH (15:9:1) yielded compound **2** (10 mg). The concd EtOAc extract yielded a ppt. of  $\beta$ -quercitrin (400 mg). The concd *n*-BuOH extract yielded a ppt. of rutin (500 mg).

*Methyl 1 $\alpha$ -acetoxyl-3 $\beta$ ,6,8 $\alpha$ -trihydroxy-2 $\alpha$ -methoxy-2 $\beta$ ,14 $\beta$ -epoxy-[4.2.1 $^{10,30}$ ,1 $^{1,4}$ ]-tricyclomeliac-7-oate (1).* Amorphous solid, mp 230–242,  $[\alpha]_{\text{D}} + 15.0$  ( $\text{CHCl}_3$ ; *c* 0.055). IR  $\nu_{\text{max}}^{\text{Film}}$   $\text{cm}^{-1}$ : 3467, 2929, 1739, 1459, 1250, 1022, 731.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): Table 1;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): Table 2; HMBC (400/100 MHz,  $\text{CDCl}_3$ ): see Table 3; NOESY-TPPI (400 MHz,  $\text{CDCl}_3$ ): Table 4. PIDCI-MS *m/z* (rel. int.): 605  $[\text{M} + \text{CH}_3]^+$  (3); 591  $[\text{M} + \text{H}]^+$  (2); 573  $[\text{M} + \text{CH}_3 - \text{CH}_3\text{OH}]^+$  (4); 559  $[\text{M} + \text{H} - \text{CH}_3\text{OH}]^+$  (2); EI-MS *m/z* (rel. int.): 447  $[\text{M} - (\text{Me} + \text{OMe} + \text{Furan-CHO} + \text{H})]^+$  (18); 446 (57); 97 (15); 95 (11); 77 (100); 69 (45); 58 (39); 57 (73).

*Methyl 1 $\alpha$ -acetoxyl-6,8 $\alpha$ ,14 $\beta$ ,30 $\beta$ -tetrahydroxy-3-oxo-[3.3.1 $^{10,2}$ ,1 $^{1,4}$ ]-tricyclomeliac-7-oate (2).* Amorphous solid, mp 280–295,  $[\alpha]_{\text{D}} + 5.8$  (DMSO; *c* 0.064). IR  $\nu_{\text{max}}^{\text{Film}}$   $\text{cm}^{-1}$ : 3358, 2949, 1733, 1455, 1250, 1019, 874.  $^1\text{H}$  NMR (400 MHz, DMSO-*d*<sub>6</sub>): Table 1;  $^{13}\text{C}$  NMR (100 MHz, DMSO-*d*<sub>6</sub>): Table 2; MS *m/z* (rel. int.): 446  $[\text{M} - (\text{CH}_2 = \text{CO} + \text{HCOCOOMe})]^+$  (100); 168 (15).

**Acknowledgements**—The authors are grateful to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação de Amparo a Pesquisa do Estado de São Paulo (FAPESP), Coordenação de Aperfeiçoamento de Pessoal de Ensino Superior (CAPES), and Financiadora de Estudos e Projetos (FINEP) for the financial support. L.R.V.O. thanks CAPES for the award of a fellowship.

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