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Professor Josep Coll Toledano  
On the Occasion of his 70th Birthday**

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## Two New Labdane-type Diterpenes from the Wood of *Cunninghamia konishii*

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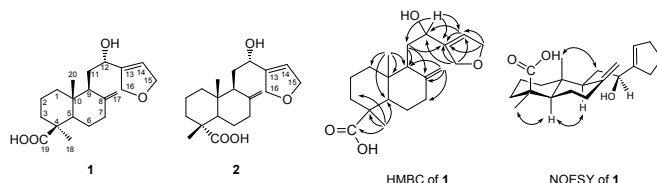
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Phytochemical investigation of the methanol extract of the wood of *Cunninghamia konishii* resulted in the isolation of two new acidic labdane-type diterpenoids, 12(*S*)-hydroxy-15,16-epoxylabda-8(17),13-dien-19-oic acid (**1**) and 12(*S*)-hydroxy-15,16-epoxylabda-8(17),13-dien-18-oic acid (**2**), along with one known labdane-type diterpene, 7,13*E*-labdadien-15-ol (**3**). Their structures were determined by analysis of spectroscopic data and comparison with the data of known analogues.

**Keywords:** Chinese herb, Taxodiaceae, *Cunninghamia konishii*, Labdane, Diterpenoid.

Two *Cunninghamia* species (Taxodiaceae) grow in eastern Asia, one of which is *C. konishii* Hayata, an endemic coniferous tree distributed in the northern and central part of Taiwan [1]. The wood of this plant exhibits soft, lightweight, aromatic, and rot-resistant properties and is thus one of the best building materials. In earlier investigations, monoterpenes, sesquiterpenes, diterpenes, and lignans were isolated from the wood, bark, leaf, and whole plant of *C. konishii* [2a-m]. Several isolates of this plant have been proven to possess anti-inflammatory [2i] and antifungal activity [2g-i], and cytotoxicity [2k]. In the continuing phytochemical investigation [2e,f,i,l,m], we further identified two new acidic labdane-type diterpenoids (**1** and **2**) (Figure 1) and one known labdane-type diterpene, 7,13*E*-labdadien-15-ol (**3**) [3a] from the wood of *C. konishii*.

Compound **1**, yellowish oil, showed IR absorption bands for a carboxylic acid, hydroxy and vinyl groups, and terminal double bonds at 3425–2520, 3394, 3078, 1692, 1647 and 895 cm<sup>-1</sup>. The resonances for a trisubstituted double bond ( $\delta_{\text{H}}$  5.80 (1H, brs);  $\delta_{\text{C}}$  120.6, 137.8), a carbinol (HOCH) group ( $\delta_{\text{H}}$  4.28 (1H, dd,  $J = 9.2, 5.6$  Hz);  $\delta_{\text{C}}$  73.1), two oxymethylenes ( $\delta_{\text{H}}$  4.51, 4.63 (each 1H, d,  $J = 13.4$  Hz), 4.63, 4.65 (each 1H, d,  $J = 13.6$  Hz);  $\delta_{\text{C}}$  69.7, 69.0), one terminal double bond ( $\delta_{\text{H}}$  4.65 (1H, brs), 4.90 (1H, brs)), and two tertiary methyls ( $\delta_{\text{H}}$  0.61, 1.22 (each 3H, s)) were observed in the <sup>1</sup>H and <sup>13</sup>C NMR spectra (Table 1). A DEPT experiment was used to differentiate 20 carbon signals as two methyl, six aliphatic methylene, two aliphatic methine, two aliphatic quaternary, two oxygenated methylene, one oxygenated methine, one olefinic methylene, one olefinic methine, two quaternary olefinic, and one carbonyl. From the above spectroscopic characteristics, compound **1** was tentatively proposed to be a labdane diterpenoid with a C<sub>6</sub>-side chain moiety on C-9. The molecular formula was deduced to be



**Figure 1:** Structures of compounds **1** and **2** and selected NOE correlations of **1**.

**Table 1:** <sup>1</sup>H and <sup>13</sup>C NMR data for **1** and **2** (400 and 100 MHz in CDCl<sub>3</sub>).

| No. | <b>1</b>            |                                   | <b>2</b>            |                                   |
|-----|---------------------|-----------------------------------|---------------------|-----------------------------------|
|     | $\delta_{\text{C}}$ | $\delta_{\text{H}}$               | $\delta_{\text{C}}$ | $\delta_{\text{H}}$               |
| 1   | 39.1 (t)            | 1.81 (m), 1.15 (m)                | 37.9 (t)            | 1.71 (m), 1.16 (m)                |
| 2   | 19.8 (t)            | 1.72 (m), 1.56 (m)                | 18.4 (t)            | 1.63 (m)                          |
| 3   | 37.8 (t)            | 2.10 (m), 1.13 (m)                | 36.9 (t)            | 2.02 (m), 1.63 (m)                |
| 4   | 44.1 (s)            |                                   | 47.4 (s)            |                                   |
| 5   | 56.1 (d)            | 1.34 (dd, 10.4, 4.8)              | 49.5 (dd)           | 1.93 (dd, 10.2, 3.5)              |
| 6   | 26.0 (t)            | 2.01 (m), 1.37 (m)                | 26.7 (t)            | 1.50 (m), 1.39 (m)                |
| 7   | 38.6 (t)            | 2.38 (m), 2.15 (m)                | 37.8 (t)            | 2.38 (m), 2.05 (m)                |
| 8   | 148.2 (s)           |                                   | 148.0 (s)           |                                   |
| 9   | 52.4 (d)            | 1.56 (t, 7.6)                     | 52.9 (d)            | 1.76 (m)                          |
| 10  | 40.3 (s)            |                                   | 38.8 (s)            |                                   |
| 11  | 29.1 (t)            | 1.78 (m)                          | 28.7 (t)            | 1.72 (m)                          |
| 12  | 73.1 (d)            | 4.28 (dd, 9.2, 5.6)               | 73.0 (d)            | 4.27 (dd, 9.2, 4.6)               |
| 13  | 137.8 (s)           |                                   | 137.7 (s)           |                                   |
| 14  | 120.6 (d)           | 5.80 (brs)                        | 120.8 (d)           | 5.80 (brs)                        |
| 15  | 69.7 (t)            | 4.63 (d, 13.4),<br>4.51 (d, 13.4) | 69.7 (t)            | 4.63 (d, 13.6),<br>4.52 (d, 13.6) |
| 16  | 69.0 (t)            | 4.65 (d, 13.6),<br>4.63 (d, 13.6) | 68.9 (t)            | 4.65 (d, 13.6),<br>4.63 (d, 13.6) |
| 17  | 107.0 (t)           | 4.90 (brs), 4.65 (brs)            | 107.6 (t)           | 4.88 (brs), 4.67 (brs)            |
| 18  | 28.9 (q)            | 1.22 (s)                          | 183.4 (s)           |                                   |
| 19  | 181.5 (s)           |                                   | 16.4 (q)            | 1.14 (s)                          |
| 20  | 12.9 (q)            | 0.61 (s)                          | 14.8 (q)            | 0.71 (s)                          |

<sup>a)</sup> Coupling constants are presented in Hz.

C<sub>20</sub>H<sub>30</sub>O<sub>4</sub> from a molecular ion at  $m/z$  334.2152 in the HR-EI-MS, which indicated six degrees of unsaturation. Five of these were attributed to the presence of a bicyclic structure, two olefins, and one C=O group, and the remaining degree of unsaturation hinted that the C<sub>6</sub>-side chain contains one additional cyclic structure. The

HMBC correlations (Figure 1) between H-14 ( $\delta_{\text{H}}$  5.80)/C-12 ( $\delta_{\text{C}}$  73.1) and C-13 ( $\delta_{\text{C}}$  137.8); H-15 ( $\delta_{\text{H}}$  4.51)/C-13 and C-14; H-16 ( $\delta_{\text{H}}$  4.65)/C-13 and C-14 aided the construction of the structure of a 3-substituted 2,5-dihydrofuran in the side chain. An  $\alpha$ -orientated hydroxy group was positioned at C-12, which was confirmed by the HMBC correlations (Figure 1) between H-12 ( $\delta_{\text{H}}$  4.28)/C-9 ( $\delta_{\text{C}}$  52.4), C-11 ( $\delta_{\text{C}}$  29.1), C-13 ( $\delta_{\text{C}}$  137.8), C-14 ( $\delta_{\text{C}}$  120.6), and C-16 ( $\delta_{\text{C}}$  69.0) and the comparison of the chemical shifts of C-12 of (12*R*)-12-hydroxyabda-8(17),13(16),14-trien-19-oic acid methyl ester ( $\delta_{\text{C}}$  69.8) and (12*S*)-12-hydroxyabda-8(17),13(16),14-trien-19-oic acid methyl ester ( $\delta_{\text{C}}$  72.2) [3b]. The significant NOE correlations between H-5 ( $\delta_{\text{H}}$  1.34)/H-9 ( $\delta_{\text{H}}$  1.56); H-5/Me-18 ( $\delta_{\text{H}}$  1.22); and H-11 ( $\delta_{\text{H}}$  1.78)/Me-20 ( $\delta_{\text{H}}$  0.61) in the NOESY spectrum (Figure 1) indicated an  $\alpha$ -orientation for H-5, H-9, and Me-18 and a  $\beta$ -orientation for H-11 and Me-20. Compound **1** showed a positive specific rotation, +21.7, consistent with that of (12*S*)-12-hydroxyabda-8(17),13(16),14-trien-19-oic acid methyl ester ( $[\alpha]_{\text{D}}^{25} = +41$ ) and was thus identified as a labdane derivative with the 12*S* configuration [4]. Accordingly, compound **1** was elucidated as (12*S*)-12-hydroxy-15,16-epoxyabda-8(17),13-dien-19-oic acid (**1**).

Compound **2** was also obtained as yellowish oil. Its HR-EI-MS showed a molecular ion peak at  $m/z$  334.2154, which corresponded to the molecular formula,  $\text{C}_{20}\text{H}_{30}\text{O}_4$ , indicating six degrees of unsaturation. The IR spectrum displayed absorption bands for carboxylic acid and hydroxy groups, and one terminal double bond at 3420–2510, 3381, 3072, 1692, 1647 and 890  $\text{cm}^{-1}$ . The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data of the side chain of **2** were found to be close to those of **1** and compound **2** was thus proposed as the 4-epimer of **1**. The COOH group was attached on C-4 in a  $\beta$  orientation, which was assured by the comparison of the chemical shifts of **2** with those of (12*S*)-12-hydroxyabda-8(17),13(16),14-trien-19-oic acid methyl ester [3b] and the significant NOE correlation between Me-19 ( $\delta_{\text{H}}$  1.14) and Me-20 ( $\delta_{\text{H}}$  0.71) in the NOESY spectrum of **2**. Thus, compound **2** was elucidated as (12*S*)-12-hydroxy-15,16-epoxyabda-8(17),13-dien-18-oic acid (**2**).

## Experimental

**Plant material:** The wood of *C. konishii* was collected at Luantashan, Nantau County, Taiwan, in December 1996 and was identified by Prof. Shao-Shun Ying, Department of Forestry, NTU. A voucher specimen (013492) has been deposited at the Herbarium of the National Taiwan University, Taipei, Taiwan.

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**Extraction and isolation:** Dried wood (6.5 kg) of *C. konishii* was crushed into pieces and extracted with MeOH (60 L) 3 times (7 days each time) at room temperature. Following removal of the solvent, the extract (60.2 g) was suspended in water (500 mL), and then partitioned into *n*-hexane (500 mL  $\times$ 3), EtOAc (500 mL  $\times$ 4), and BuOH (500 mL  $\times$ 3), successively. The EtOAc fraction (15.6 g) was subjected to a silica gel (450 g) column using *n*-hexane–EtOAc and EtOAc–MeOH mixtures as solvent systems to obtain 11 fractions. HPLC of fr. 6 from *n*-hexane/EtOAc (1/1) elution on a Merck LiChrosorb Si 60 column with  $\text{CH}_2\text{Cl}_2$ –acetone–*i*-PrOH (10:1:0.2) as eluent yielded **1** (2.2 mg). Fr. 7 from *n*-hexane–EtOAc (3:2) elution was further purified by HPLC to give **2** (3.1 mg) using *n*-hexane– $\text{CH}_2\text{Cl}_2$ –EtOAc–*i*-PrOH (6:3:1:0.2). Fr. 4 from *n*-hexane–EtOAc (7:3) elution was further purified by HPLC to give **3** (2.5 mg) using *n*-hexane– $\text{CH}_2\text{Cl}_2$ –EtOAc–*i*-PrOH (8:2:1:0.2).

### 12(*S*)-Hydroxy-15,16-epoxyabda-8(17),13-diene-19-oic acid (**1**)

Yellowish oil.  
 $[\alpha]_{\text{D}}^{27}$ : +21.7 ( $c$  0.20,  $\text{CHCl}_3$ ).  
 IR: 3425–2520, 3394, 3078, 1692, 1647, 1383, 1034, 895  $\text{cm}^{-1}$ .  
 $^1\text{H}$  and  $^{13}\text{C}$  NMR: Table 1.  
 EI-MS  $m/z$  (rel. int.): 334 [ $\text{M}]^+$  (2), 333 (22), 332 (100), 316 (32), 314 (81), 288 (21), 286 (19), 266 (17).  
 HR- EI-MS:  $m/z$  334.2152 (calcd for  $\text{C}_{20}\text{H}_{30}\text{O}_4$  334.2145, [ $\text{M}]^+$ ).

### 12(*S*)-Hydroxy-15,16-epoxyabda-8(17),13-diene-18-oic acid (**2**)

Yellowish oil.  
 $[\alpha]_{\text{D}}^{27}$ : +10.3 ( $c$  0.28,  $\text{CHCl}_3$ ).  
 IR: 3420–2510, 3381, 3072, 1692, 1647, 1383, 1047, 890  $\text{cm}^{-1}$ .  
 $^1\text{H}$  and  $^{13}\text{C}$  NMR: Table 1.  
 EI-MS  $m/z$  (rel. int.): 334 [ $\text{M}]^+$  (2), 332 (9), 314 (21), 301 (22), 288 (17), 175 (38), 121 (100).  
 HR- EI-MS:  $m/z$  334.2154 (calcd for  $\text{C}_{20}\text{H}_{30}\text{O}_4$  334.2145, [ $\text{M}]^+$ ).

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|  |      |
|--|------|
| <b>Evaluation of Anti-melanoma Activities of (1S,2E,4R,6E,8R,11S,12R)-8,12-epoxy-2,6-cembradiene-4,11-diol, (1S,2E,4R,6E,8S,11R,12S)-8,11-epoxy-4,12-epoxy-2,6-cembradiene and (1S,4R,13S)-cembra-2E,7E,11E-trien-4,13-diol from the Red Sea soft coral <i>Sarcophyton glaucum</i></b> |      |
| Pawel T. Szymanski, Safwat A. Ahmed, Mohamed M. Radwan, Sherief I. Khalifa and Hesham Fahmy  | 1143 |
| <b>Spiculisporic Acid E, a New Spiculisporic Acid Derivative and Ergosterol Derivatives from the Marine-Sponge Associated Fungus <i>Talaromyces trachyspermus</i> (KUFA 0021)</b>  |      |
| Decha Kumla, Tida Dethoup, Suradet Buttachon, Narong Singburadom, Artur M.S. Silva and Anake Kijjoa  | 1147 |
| <b>Chemical Composition of Bioactive Alkaloid Extracts from Some <i>Narcissus</i> Species and Varieties and their Biological Activity</b>  |      |
| Jana Havlasová, Marcela Šafratová, Tomáš Siatka, Šárka Štěpánková, Zdeněk Novák, Miroslav Ločárek, Lubomír Opletal, Martina Hrabínová, Daniel Jun, Nina Benešová, Jiří Kuneš and Lucie Cahlíková   | 1151 |
| <b>Quantitative Determination of Lycorine and Galanthamine in <i>Galanthus trojanus</i> and <i>G. cilicicus</i> by HPLC-DAD</b>  |      |
| Gulen Irem Kaya, Derya Cicek Polat, Buket Sarikaya, Mustafa Ali Onur and Nehir Unver Somer   | 1157 |
| <b>Anthranilic Acid Derivatives and Other Components from <i>Ononis pusilla</i></b>  |      |
| Lyes Khouni, Christophe Long, Hamada Haba, Nicolas Molinier and Mohammed Benkhaled   | 1159 |
| <b>Trigonelline Accumulation in Leaves of <i>Panicum virgatum</i> Seedlings</b>  |      |
| Lauren M. Schwartz, Andrew J. Wood and David J. Gibson   | 1163 |
| <b>New Phenylpropanoid-Substituted Flavan-3-ols from Pu-er Ripe Tea</b>  |      |
| Mu-Ke Tao, Min Xu, Hong-Tao Zhu, Rong-Rong Cheng, Dong Wang, Chong-Ren Yang and Ying-Jun Zhang   | 1167 |
| <b>Parvisides A and B, New Glucosides from <i>Galinsoga parviflora</i></b>   |      |
| Nighat Afza, Abdul Malik, Shazia Yasmeen, Muhammad Irfan Ali, Sadia Ferheen and Rasool Bakhsh Tareen   | 1171 |
| <b>Structure Activity Relationships of Flavonoids as Potent <math>\alpha</math>-Amylase Inhibitors</b>   |      |
| Erdong Yuan, Benguo Liu, Qingyi Wei, Jiguo Yang, Lei Chen and Qiong Li   | 1173 |
| <b>Two New Anxiolytic Phenanthrenes Found in the Medullae of <i>Juncus effusus</i></b>   |      |
| Yang Wang, Gui-Yun Li, Qian Fu, Tai-Sen Hao, Jian-Mei Huang and Hai-Feng Zhai  | 1177 |
| <b>A New Depside from <i>Usnea aciculifera</i> Growing in Vietnam</b>  |      |
| Tuong L. Truong, Vo T. Nga, Duong T. Huy, Huynh B. L. Chi and Nguyen K. P. Phung   | 1179 |
| <b>Chemical Analysis of Volatile Oils from West Himalayan Pindrow Fir <i>Abies pindrow</i></b>   |      |
| Rajendra C. Padalia, Ram S. Verma, Amit Chauhan, Prakash Goswami and Chandan S. Chanotiya  | 1181 |
| <b>Characterization of Volatiles of Necrotic <i>Stenocereus thurberi</i> and <i>Opuntia littoralis</i> and Toxicity and Olfactory Preference of <i>Drosophila melanogaster</i>, <i>D. mojavensis wrighti</i>, and <i>D. mojavensis sonorensis</i> to Necrotic Cactus Volatiles</b>     |      |
| Cynthia R. Wright and William N. Setzer  | 1185 |
| <b><u>Accounts/Reviews</u></b>   |      |
| <b>Cytotoxicity Studies of Lycorine Alkaloids of the Amaryllidaceae</b>  |      |
| Jerald J. Nair and Johannes van Staden   | 1193 |
| <b>Warfarin Interactions with Medicinal Herbs</b>  |      |
| Nataša Milić, Nataša Milošević, Svetlana Goločorbin Kon, Teodora Božić, Ludovico Abenavoli and Francesca Borrelli  | 1211 |
| <b>Acemannan, an Extracted Polysaccharide from <i>Aloe vera</i>: A Literature Review</b>   |      |
| Gerardo Daniel Sierra-García, Rocío Castro-Rios, Azucena González-Horta, Jorge Lara-Arias and Abelardo Chávez-Montes   | 1217 |



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### Volume 9, Number 8

#### Contents

#### Articles dedicated to Prof. Josep Coll Toledano on the Occasion of his 70<sup>th</sup> Birthday

| <u>Original Paper</u>  | <u>Page</u> |
|--|-------------|
| <b>Sesquiterpene Hydrocarbons from the Liverwort <i>Treubia isignensis</i> var. <i>isignensis</i> with Chemotaxonomic Significance</b><br>Paul Coulerie, Mohammed Nour, Louis Thouvenot and Yoshinori Asakawa  | 1059        |
| <b>Microbial Transformation of the Diterpene 7-<i>epi</i>-Foliol by <i>Fusarium fujikuroi</i></b><br>Braulio M. Fraga, Carlo Bressa, Pedro González and Ricardo Guillermo  | 1061        |
| <b><sup>1</sup>H and <sup>13</sup>C NMR Analysis of the <i>neo</i>-Clerodane Diterpenoid Scuteceyprin</b><br>Plamen N. Penchev, Stefka R. Nachkova, Tonka A. Vasileva and Petko I. Bozov   | 1065        |
| <b>Ecdysteroid Profiles of Two <i>Ajuga</i> species, <i>A. iva</i> and <i>A. remota</i></b><br>Ahmed Bakrim, Johnpeter Ngunjiri, Sophie Crouzet, Louis Guibout, Christine Balducci, Jean-Pierre Girault and René Lafont  | 1069        |
| <b>Antiparasitic Indole Alkaloids from <i>Aspidosperma desmanthum</i> and <i>A. spruceanum</i> from the Peruvian Amazonia</b><br>Matías Reina, Lastenia Ruiz-Mesia, Wilfredo Ruiz-Mesia, Frida Enriqueta Sosa-Amay, Leonor Arevalo-Encinas, Azucena González-Coloma and Rafael Martínez-Díaz | 1075        |
| <b>Analysis of Bioactive Amaryllidaceae Alkaloid Profiles in <i>Lycoris</i> Species by GC-MS</b><br>Ying Guo, Natalia B. Pigni, Yuhong Zheng, Jean Paulo de Andrade, Laura Torras-Claveria, Warley de Souza Borges, Francesc Viladomat, Carles Codina and Jaume Bastida                      | 1081        |
| <b>Mechanistic Studies on the Intramolecular Cyclization of <i>O</i>-Tosyl Phytosphingosines to Jaspines</b><br>Ramón Crehuet, David Mormeneo, Josep M. Anglada and Antonio Delgado  | 1087        |
| <b>Chemistry and Biological Activity of Coumarins at Molecular Level</b><br>Hugo A. Garro, Celina García, Víctor S. Martín, Carlos E. Tonn and Carlos R. Pungitore   | 1091        |
| <b>Chemoenzymatic Solvent-free Synthesis of 1-Monopalmitin Using a Microwave Reactor</b><br>Rubén Torregrosa, Mercé Balcells, Mercé Torres and Ramon Canela-Garayoa  | 1095        |
| <b>EAG Responses Increase of <i>Spodoptera littoralis</i> Antennae after a Single Pheromone Pulse</b><br>Carmen Quero, Berta Vidal and Angel Guerrero  | 1099        |
| <b>Cuticular and Internal Chemical Composition of Biting Midges <i>Culicoides</i> spp. (Diptera: Ceratopogonidae), Potential Vectors of Viral Diseases</b><br>Mikel González, Sergio López, Gloria Rosell, Arturo Goldarazena and Angel Guerrero   | 1103        |
| <b>Valorization of Essential Oils from Moroccan Aromatic Plants</b><br>Omar Santana, María Fe Andrés, Jesús Sanz, Naima Errahmani, Lamiri Abdeslam and Azucena González-Coloma   | 1109        |
| <b>A List of and Some Comments about the Trail Pheromones of Ants</b><br>Kim Cerdá, Louise van Oudenhove, Carlos Bernstei and Raphaël R. Boulay  | 1115        |
| -----  |             |
| <b>New Pseudoguaiane Derivatives from <i>Inula aschersoniana</i> Janka var. <i>aschersoniana</i></b><br>Antoaneta Trendafilova, Milka Todorova, Viktoriya Genova, Pavletta Shestakova, Dimitar Dimitrov, Milka Jadrantin and Slobodan Milosavljevic  | 1123        |
| <b>A New Sesquiterpene Glucoside from <i>Lysionotus pauciflorus</i></b><br>Yaya Wen, Hongjian Du, Yanbei Tu, Wei Luo, Qin Li, Yanfang Li and Bing Liang  | 1125        |
| <b>Two New Labdane-type Diterpenes from the Wood of <i>Cunninghamia konishii</i></b><br>Chi-I Chang, Yen-Cheng Li, Che-Yi Chao, Sheng-Yang Wang, Hsun-Shuo Chang, Louis Kuoping Chao, Chang Syun Yang and Yueh-Hsiung Kuo  | 1127        |
| <b>Antibacterial activity of <i>Taxodium ascendens</i> Diterpenes against Methicillin-resistant <i>Staphylococcus aureus</i></b><br>Courtney M. Starks, Vanessa L. Norman, Russell B. Williams, Matt G. Goering, Stephanie M. Rice, Mark O'Neil-Johnson and Gary R. Eldridge                 | 1129        |
| <b>Use of Circular Dichroism to Determine the Absolute Configuration of a Pimarane Diterpenoid from the Southern African <i>Sclerocroton integerrimus</i> (Euphorbiaceae)</b><br>Vuyelwa J. Tembu, Moses K. Langat, Neil R. Crouch and Dulcie A. Mulholland                                  | 1131        |
| <b>Isolation and Structure Elucidation of Rebaudioside D2 from Bioconversion Reaction of Rebaudioside A to Rebaudioside D</b><br>Indra Prakash, Cynthia Bunders, Krishna P. Devkota, Romila D. Charan, Catherine Ramirez, Maunik Parikh and Avetik Markosyan                                 | 1135        |
| <b>2-Acetoxyverecynarmin C, a New Briarane COX Inhibitory Diterpenoid from <i>Pennatula aculeata</i></b><br>Anu Bahl, Sanjay M. Jachak, Kishneth Palaniveloo, Tulasiraman Ramachandram, Charles S. Vairappan and Harish K. Chopra  | 1139        |

Continued inside backcover