Protecting-group-free Synthesis of Cassane Type Furan Diterpenes *via* a Decarboxylative Dienone-Phenol Rearrangement

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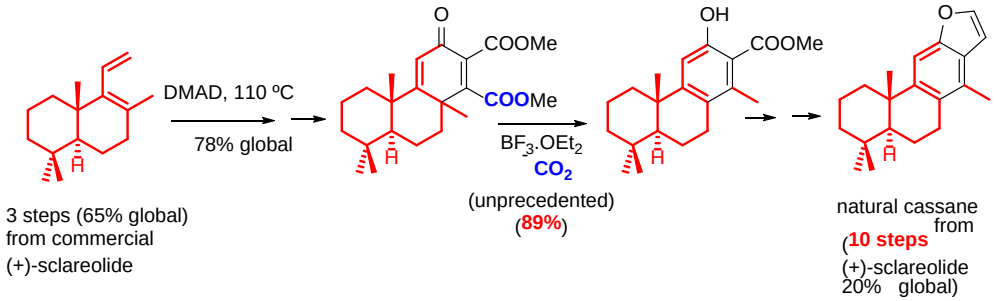
Supporting Information Placeholder

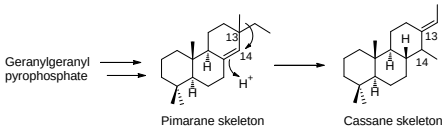


ABSTRACT: An expeditious route to obtaining cassane-type furan diterpenes starting from (+)-sclareolide, an inexpensive commercially available natural lactone, has been achieved by using a solvent-free Diels-Alder cycloaddition and an unprecedented decarboxylative dienone-phenol rearrangement as key steps. Its applicability is showcased by the first synthesis of (5α)-vouacapane-8(14),-9(11)-diene. The synthesis, which requires no protecting group, is efficient, and atom- and step-economical (10 steps, 20 % global).

Organic synthesis, in addition to its main objective of preparing compounds of interest, is increasingly following the principles of sustainable chemistry, such as the use of renewable starting products, whose representatives are natural products,[1] and the utilization of atom-economical synthetic sequences,[2] using protecting-group-free[3] and tandem reactions.[4] With the above premises in mind, we have developed a synthetic strategy towards cassane-type furan diterpenes from the abundant feedstock chemical (+)-sclareolide (**20**). This inexpensive commercially available terpene lactone is a versatile synthon for the preparation of diverse natural products. In the past decade, many important new methods for its chemical and biological transformation have been reported in the literature.[5] Recently reported procedures for the regioselective functionalization of the A ring of this lactone, in a single step, have considerably increased the synthetic potential of this compound, facilitating the preparation of sufficient quantities of target compounds for the investigation of its biological and medical properties.[6]

Natural cassane diterpenes[7] are a group of diterpenoid substances which are well-known for their wide range of pharmacological activities, with anti-tumoral,[8] anti-malarial,[9] anti-inflammatory,[10] anti-viral,[11] anti-microbial[12] and anti-trypanosomal effects.[13] The basic cassane skeleton is structurally characterized as a tricyclic diterpene with a substitution of the ethyl group at C-13 and of a methyl group at C-14. It is considered to be derived from the pimarane diterpene skeleton by methyl migration from C-13 to C-14 (Scheme 1).[14]

Scheme 1. Biosynthetic pathway proposed for cassane diterpenes



The ethyl group at C-13 is usually part of a fourth furane or lactone cycle, the C ring being aromatic in some cases, within cassane diterpenes. These compounds frequently present a high degree of functionality. Representative examples are caesaldekarin A (**1**), which inhibits the production of interleukin-1,[15] 14-deoxy-ε-caesalpin (**2**),[16] sucutirinane B (**3**),[17] neocaesalpin D (**4**),[18] demethylcaesaldekarin C (**5**), the hydroxyfuran **7**,[19] which exerts a potent anti-inflammatory activity,[20] the anti-malarial 2-acetoxycaesaldekarin E (**8**)[21] and caesalpin D (**9**), with selective cytotoxic activities against MCF-7 and AGS human cancer cell lines.[22] Other remarka-

ble compounds are taepeenin D (**10**), an effective inhibitor of the Hedgehog/GLI signaling pathway, that therefore may be valuable as a probe of diseases related to Hh/GLI-dependent cancer, and related compounds (**11-13**),[23] taepeenin F (**14**),[23a] the anti-bacterial benthaminin 1 (**15**)[24] and benthaminin 3 (**16**)[25](Figure 1).

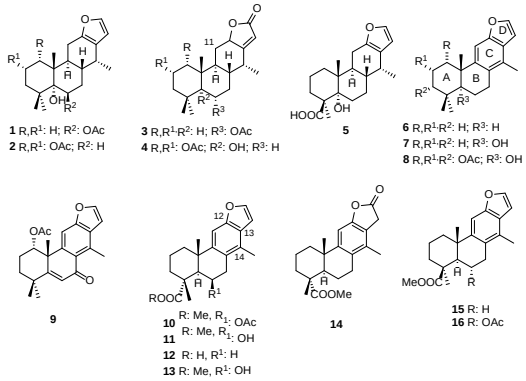
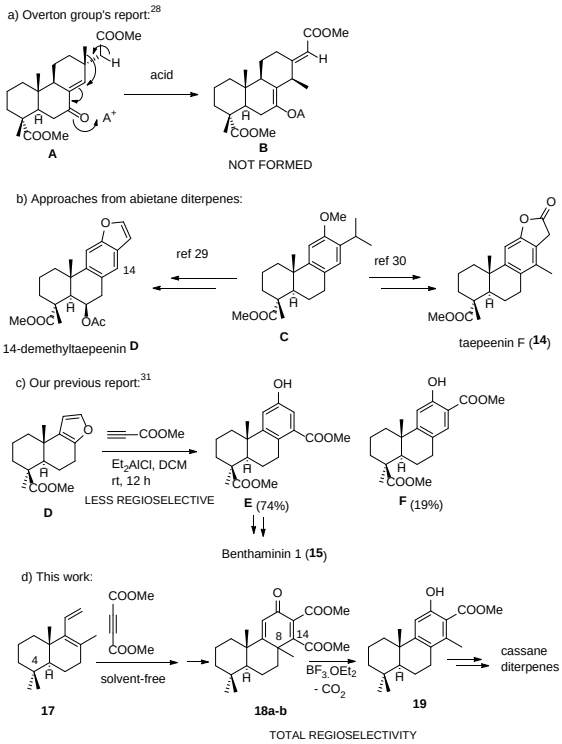


Figure 1. Some representative cassane-type diterpenes.

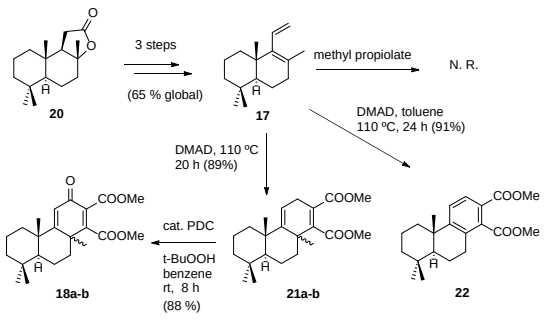
Little is known about the synthesis of this type of compounds, despite the interest they have aroused due to its wide and varied activity. Only a few syntheses,[26] and related synthetic studies,[27] have been reported. In regard to the synthesis of cassane diterpenes from structurally-related natural products, several alternatives have been proposed. An initial possibility, which seems plausible, is that of C13 to C14 methyl migration on a pimarane precursor, following the biosynthetic pathway. However, attempts to achieve this transformation have proven to be unsuccessful. Thus, Overton et al. reported that the pimarane ketoester **A** does not achieve the desired rearrangement under different acid conditions (Scheme 2).[28] At first sight, abietane diterpenes might also be considered suitable precursors of cassane diterpene, in view of their structural relationship. In this respect, Pitsinos et al. recently described the synthesis of the 14-demethyl derivative of taepeenin D (**7**), via dehydroabietane **C**, which is easily prepared from abietic acid.[29] Very recently, our group has described the introduction of the methyl group at the C-14 position of dehydroabietane derivatives (18 steps from abietic acid).[30] A few years before, our research group had described the first enantiospecific synthesis of a cassane benzofuran, benthaminin 1 (**15**), starting from the labdane diterpene *trans*-communic acid.[31] The key step in this synthesis was a Diels-Alder/aromatization sequence of the furan sesquiterpene **D** with methyl propiolate, which afforded, with moderate regioselectivity, the isomer **E**, a precursor of cassane **15**. In the present paper, we propose the introduction of a methyl group at C-14, through a dienone-phenol rearrangement of compound **18a-b**, with simultaneous decarboxylation, which affords the cassane precursor **19**, with complete regioselectivity.

Taking into account the above arguments, we planned the synthesis of (5α)-vouacapane-8(14),-9(11)-diene (**6**), a cassane furan that has not yet been synthesized, from commercial (+)-sclareolide (**20**). The furan diterpenoid **6** can be utilised as a marker to chemically differentiate two species of the vegetal genus *Caesalpinia*.[32]

Scheme 2. Approaches to the cassane skeleton from terpenoids.



Scheme 3. Synthesis of dienone 18a-b from commercial (+)-sclareolide (20).

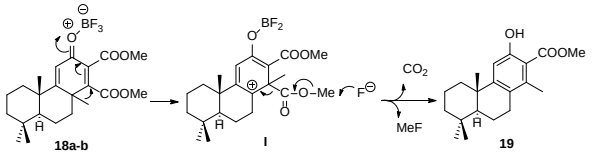


Scheme 3 shows the synthesis of dienone **18a-b** from (+)-sclareolide (**20**). After the synthesis of diene **17** from lactone **20**, following a three-step sequence developed in our laboratory,[33] and subsequently employed by other groups,[34] the Diels-Alder cycloaddition of this diene was investigated. First, the reaction with methyl propiolate was considered; however, no reaction was obtained under any of the experimental conditions, including the use of pressure and of Lewis acids. We then considered the use of dimethyl acetylenedicarboxylate (DMAD) as the dienophile. When the reaction was performed in toluene under reflux, the phthalate derivative **22** was obtained in good yield after 24 h (see the Supporting Infor-

mation (SI)), and when diene **17** was heated with DMAD in a sealed tube at 110 °C for 20 h, the desired cycloadduct **21a-b** was obtained, as a 9:1 mixture of 8-epimers.[35] The next step was to achieve the oxidation of this cycloadduct. After tests under different reaction conditions, ketone **18a-b** was obtained in good yield after reaction with catalytic PDC in benzene.

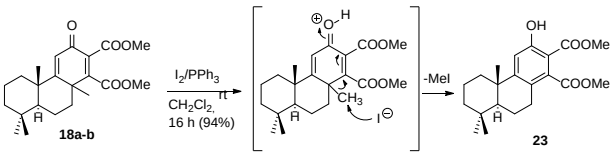
Next, the dienone-phenol rearrangement was investigated. After essaying the treatment of dienone **18a-b** under different acid conditions, the migration of the methyl group and simultaneous decarboxylation, took place when dienone **18a-b** was treated with $AlCl_3$, $AlBr_3$ or $BF_3.OEt_2$ in dichloromethane at room temperature, affording hydroxyester **19**. The best results were obtained with $BF_3.OEt_2$ in CH_2Cl_2 at room temperature for 15 h. No reaction took place when protic acids, as TsOH and TfOH, and other Lewis acids, as $Bi(OTf)_3$ and $Sc(OTf)_3$, in CH_2Cl_2 under reflux were utilized. The treatment with BI_3 in CH_2Cl_2 at room temperature gave a complex mixture (see the SI)). A possible mechanism for this unprecedented reaction[36] is postulated in Scheme 4. The ion fluoride attack on the methyl ester group facilitates the decarboxylation and aromatization process in the carbocation **I**.

Scheme 4. A possible mechanism for the dienone-phenol rearrangement, with simultaneous decarboxylation.



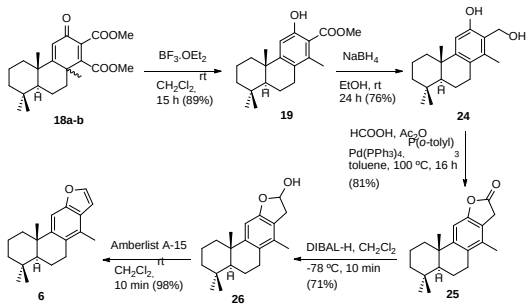
Interestingly, hydroxy ester **23** was obtained in high yield. when dienone **18a-b** was treated with I_2/PPh_3 (see the SI). This compound resulted after the attack of the HI generated in the reaction medium (Scheme 5).

Scheme 5. Formation of hydroxy ester 23 after treatment of dienone 18a-b with I_2/PPh_3.



Finally, hydroxyester **19** was transformed into the target cassane diterpene **6** (Scheme 6). Lactone **25** was obtained after the insertion of carbon monoxide in the hydroxy phenol **24**, through a Pd-catalyzed carbonylative reaction.[37] The further reduction of lactone with DIBAL-H gave lactol **26**, together with a small quantity of the corresponding *o*-hydroxyethyl phenol (see the SI), also easily transformable into the target compound. Finally, the dehydration of compound **26** gave natural (5α)-vouacapane-8(14),-9(11)-diene (**6**), not yet synthesized. Compound **6** was obtained as a white solid (mp 50-51°C; lit. [30]: mp 48 °C), presenting an optical rotation ($[\alpha]_D^{25}$ = + 48.2 (c 0.2, $CHCl_3$)). The spectroscopic properties of compound **6** were identical to those reported in the literature.[32]

Scheme 6. Synthesis of cassane 6 from dienone 18a-b.



The strategy described in this paper could be used to synthesize, in just a few steps, a wide variety of cassane-type diterpenoids, including those with a cyclohexane C ring, such as cassane similar to compounds **1-5**, which should be accessible after hydrogenation of the corresponding lactones or lactols that are precursors of benzofuranes. The above sequence might also be applicable to the synthesis of cassane diterpenes functionalized in the A ring, starting from A ring-functionalized (+)-sclareolide, which can be easily obtained in one step,[6] or utilizing dienes similar to compound **17**, bearing a carboxylate group at C-4, which could be synthesized from the suitable diterpene acid, such as the naturally abundant *trans*-communic acid,[31] or abietic acid.[38] The dienone-phenol rearrangement described here might also be aplicable to the synthesis of other natural terpenes.[39]

In summary, the first synthesis of (5α)-vouacapane-8(14),-9(11)-diene (**6**), a natural cassane-type furan diterpene, from the commercially available lactone (+)-sclareolide (**20**), is reported. The efficient synthetic sequence, involving solvent-free Diels-Alder cycloaddition and an unprecedented decarboxylative dienone-phenol rearrangement, is protecting-group-free and atom- and step-economical (10 steps, 20% global). This procedure can be employed to achieve the synthesis of a wide variety of cassane diterpenes and other terpenoids.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:
Experimental procedures, product characterizations and ^1H and ^{13}C NMR spectra for all new compounds.

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Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Natural products can be considered as typical renewable starting materials. For reviews concerning syntheses from natural products, see: *(*a) Salazar, F. J.; Villamizar, J. E. *J. Chem. Res*. **2013**, *37*, 63-70. (b) Frija, L. M. T.; Frade, R. F. M.; Afonso, C. A. M. *Chem. Rev*. **2011**, *111*, 4418-4452. (c) Kunz, H.; Hofmeister, A.; Glaser, B. *Polysaccharides* **1998**, 539-567. (d) Pelyvas, I. F.; Thiem, J.; Toth, J. Z. G. *J. Carbohyd. Chem.* **1998**, *17*, 1-26.

(2) For selected examples, see: (a) Zhou, Q.; Hong, X.; Cui, H.-Z.; Huang, S.; Yi, Y.; Hou, X.-F. *J. Org. Chem.* **2018**, *83*, 6363-6372. (b) Tang, S.-B.; Zhang, X.; Tu, H.-F.; You, S.-L. *J. Am. Chem. Soc.* **2018**, *140*, 7737-7742.

(3) For selected examples, see: (a) Halle, M. B.; Yudhistira, T.; Lee, W.-H.; Mulay, S. V.; Churchill, D. G. *Org. Lett.* **2018**, *20*, 3557-3561. (b) Sabatini, M. T.; Karaluka, V.; Lanigan, R. M.; Boulton, L. T.; Badland, M.; Sheppard, T. D. *Chem. Eur. J.* **2018**, *24*, 7033-7043. (c) Hoffmann, G.; Studer, A. *Org. Lett.* **2018**, *20*, 2964-2966.

(4) For a recent review, see: Huang, Y.-B.; Liang, J.; Wang, X.-S.; Cao, R. *Chem. Soc. Rev*. **2017**, *46*, 126-157.

(5) For a recent review concerning the chemical manipulation and biotransformation of (+)-sclareolide (**20**), see: Frija, L. M. T.; Frade R. F. M.; Afonso C. A. M. *Chem. Rev*. **2011**, *111*, 4418-4452.

(6) (a) Laudadio, G.; Govaerts, S.; Wang, Y.; Ravelli, D.; Koolman, H. F.; Fagnoni, M.; Djuric, S. W.; Noji, T. *Angew. Chem. Int. Ed.* **2018**, *57*, 4078-4082. (b) Kawamata, Y.; Yan, M.; Liu, Z.; Bao, D. -H.; Chen, J. ; Starr, J. T.; Baran, P. S. *J. Am. Chem. Soc*. **2017**, *139*, 7448-7451. (c) Hall, E. A.; Sarkar, M. R.; Lee, J. H. Z.; Munday, S. D.; Bel, S. G. *ACS Catal*. **2016**, *6*, 6306-6317. (d) Czaplyski, W. L.; Na, C. G.; Alexanian, E. J. *J. Am. Chem. Soc*. **2016**, *138*, 13854-13857. (e) Canta, M.; Font, D.; Gómez, L.; Ribas, X.; Costas, M. *Adv. Synth. Catal*. **2014**, *356*, 818-830.

(7) For seminal reviews, see: (a) Bao, H.; Zhang, Q.; Ye, Y.; Lin, L. *Phytochem. Rev*. **2017**, *16*, 235-270. (b) Maurya, R.; Ravi, M.; Singh, S.; Yadav, P. P. *Fitoterapia* **2012**, *83*, 272-280. (c) Dickson, R. A.; Fleischer, T. C.; Houghton, P. J. *Pharmacognosy* **2011**, *1*, 63-77.

(8) (a) Yodsaoue, O.; Karalai, C.; Ponglimanont, C.; Tewtrakui, S.; Chantrapromma, S. *Phytochemistry* **2010,** *71*, 1756-1764. (b) Yodsaoue, O.; Cheenpracha, S.; Karalai, C.; Ponglimanont, C.; Chantrapromma, S.; Fun, H.-K.; Kanjana-Opas, A. *Phytochemistry* **2008**, *69*, 1242-1249. (c) Udenigwe, C. C.; Ata, A.; Samarasekera, R. *Chem. Pharm. Bull*. **2007**, *55*, 442-445.

(9) (a) Kalauni, S. K.; Awale, S.; Tezuka, Y.; Banskota, A. H.; Linn, T. Z.; Asih, P. B. S.; Syafrunddin, D.; Kadota, S. *Biol. Pharm. Bull.* **2006**, *29*, 1050-1052. (b) Linn, T. Z.; Awale, S.; Tezuka, Y.; Banskota, A. H.; Kalauni, S. K.; Attamimi, F.; Ueda, J. Y.; Asih, P. B.; Syafruddin, D.; Tanaka, K.; Kadota, S. *J. Nat. Prod.* **2005**, *68*, 706-710.

(10) (a) Xiang, G.; Fan, M.; Ma, Y.; Wang, M.; Gao, J.; Chen, J.; Li, X.; Xue, W.; Wang, Y.; Gao, H.; Shen, Y.; Xu, Q. *Biochem. Pharmacol.* **2018**, *150*, 150-159. (b) Mitsui, T.; Ishihara, R.; Hayashi, K.-I.; Sunadome, M.; Matsuura, N.; Nozaki, H. *Chem. Pharm. Bull.* **2014**, *62*, 267-273.

(11) (a) Jiang, R.-W.; Ma, S.-C.; He, Z.-D.; Huang, X.-S.; But, P. P. H.; Wang, H.; Chan, S.-P.; Ooi, V. E.-C.; Xu, H.-X.; Mak, T. C. W. *Bioorg. Med. Chem.* **2002**, *10*, 2161-2170. (b) Jiang, R.-W.; But, But, P. P. H.; Ma, S.-C.; Ye, W.-C.; Chan, S.-P.; Mak, T. C. W.; *Tetrahedron Lett.* **2002**, *43*, 2415-2418.

(12) (a) Sudhakar, C.; Reddy, P. R.; Raju, T. V.; Das, B. *Tetrahedron Lett*. **2012**, *53*, 3850-3852. (b) Ragasa, C. Y.; Hofilena, J. G.; Rideout, J. A. *J. Nat. Prod*. **2002**, *65*, 1107-1110.

(13) (a) Mendoza, D. T.; Gonzalez, L. U. D.; Barria, E. O. *J. Nat. Prod*. **2004**, *67*, 1711-??. (b) Mendoza, D. T.; Gonzalez, L. U. D.; Barria, E. O.; Capson, T. L.; Rios, L. C. *J. Nat. Prod*. **2003**, *66*, 928-932.

(14) Overtone, K. H. Terpenoids and steroids, vol 4, Chemical Society (Great Britain), **1974**.

(15) Kitagawa, I.; Partomuan, S.; Watano, T.; Shibuya, H.; Fujii, S.; Yamagata, Y.; Kobayashi, M. *Chem. Pharm Bull*. **1994**, *42*, 1798-1802.

(16) Roengsumran, S.; Limsuwankesorn, S.; Ngamrojnavanich, N.; Petsom, A.; Chaichantipyuth, C.; Ishikawa, T. *Phytochemistry* **2000**, *53*, 841-844.

(17) Matsuno, Y.; Deguchi, J.; Hirasawa, Y.; Ohyama, K.; Toyoda, H.; Hirobe, C.; Ekasari, W.; Widyawaruyanti, A.; Zaini, N. C.; Morita, H. *Bioorg. Med. Chem. Lett*. **2008**, *18*, 3774-3777.

(18) Kinoshita, T. *Chem. Pharm. Bull*. **2000**, *48*, 1375-1377.

(19) Lyder, D. L.; Peter, S. R.; Tinto, W. F.; Bissad, S. M.; McLean, S.; Reynolds, W. F. *J. Nat. Prod*. **1998**, *61*, 1462-1465.

(20) (a) McPherson, D. D.; Che, C.-T.; Cordell, G. A.; Soejarto, D. D.; Pezzuto, J. M.; Fong, H. H. S. *Phytochemistry* **1986**, *25*, 167-170. (b) Yodsaoue, O.; Karalai, C.; Ponglimanont, C.; Tewtrakul, S.; Chantrapromma, S. *Tetrahedron* **2011**, *67*, 6838-6846.

(21) (a) Pascoe, K. O.; Burke, B. A.; Chan, W. R. *J. Nat. Prod*. **1986**, *49*, 913-915. (b) Linn, T. Z.; Awale, S.; Tezuka, Y.; Banskota, A. H.; Kalauni, S. K.; Attamimi, F.; Ueda, J.; Asih, P. B. S.; Syafruddin, D.; Tanaka, K.; Kadota, S. *J. Nat. Prod*. **2005**, *68*, 706-710.

(22) Ma, G.; Yuan, J.; Wu, H. ; Cao, L. ; Zhang, X.; Xu, L.; Wei, H.; Wu, L.; Zheng, Q.; Li, L.; Zhang, L.; Yang, J.; Xu, X. *J. Nat. Prod.* **2013**, *76*, 1025-1031.

(23) (a) Cheenpracha, S.; Srisuwan, R.; Karalai, C.; Ponglimanont, C.; Chantrapromma, S.; Chantrapromma, K.; Fun, H. K.; Anjum, S.; Atta-ur-Rahman, S. *Tetrahedron* **2005**, *61*, 8656-8662. (b) Rifai, Y.; Arai, M. A.; Koyano, T.; Kowithayakorn, T.; Ishibashi, M. J. *J. Nat. Prod*. **2010**, *73*, 995-997.

(24) Dickson, R. A.; Houghton, P. J.; Hylands, P. J. *Phytochemistry* **2007**, *68*, 1436-1441.

(25) Dickson, R. A.; Annan, K.; Fleischer, T. C.; Houghton, P. J. *J. Pharmacognosy Nutr. Sc*. **2012**, *2*, 21-26.

(26) (a) Yajima, A.; Mori, K. *Eur. J. Org. Chem.* **2000**, 4079-4091. (b) Spencer, T. A.; Villarica, R. M.; Storm, D. L.; Weaver, T. D.; Friary, R. J.; Posler, J.; Shafer, P. R. *J. Am. Chem. Soc*. **1967**, *89*, 5497-5499. (c) Spencer, T. A.; Smith, R. A. J.; Storm, D. L.; Villarica, R. M. *J. Am. Chem. Soc*. **1971**, *93*, 4856-4864. (d) Bernasconi, S.; Gariboldi, P.; Jommi, G.; Sisti, M.; Tavecchia, P. *J. Org. Chem.* **1981**, *46*, 3719-3721. (e) Wang, F.; Chiba, K.; Tada, M. *Chemistry Lett.* **1993**, 2117-2120. (f) Huang, J.; Foyle, D.; Lin, X.; Yang, J. *J. Org. Chem.* **2013**, *78*, 9166-9173.

(27) (a) Nakazawa, Y.; Nagatomo, M.; Oikawa, T.; Oikawa, M.; Ishikawa, Y. *Tetrahedron Lett.* **2016**, *57*, 2628-2630. (b) Tzouma, E.; Mavridis, I.; Vidali, V. P.; Pitsinos, A. N. *Tetrahedron Lett.* **2016**, *57*, 3643-3647.

(28) Johnston, J. P.; Overton, K. H. *J. Chem. Soc*. **1973**, 853-858.

(29) Chatzopoulou, M.; Antoniou, A.; Pitsinos, E. N.; Bantzi, M.; Koulocheri, S. D.; Haroutounian, S. A.; Giannis, A. *Org. Lett*. **2014**, *16*, 3344-3347.

(30) Gutierrez, P.; Altarejos, J.; Linares-Palomino, P. J.; Chahboun, R.; Alvarez-Manzaneda, E. *Org. Chem. Front.* **2018**, *5*, 2537-2541.

(31) Mahdjour, S.; Harche-Kaid, M.; Haidour, A.; Chahboun, R.; Alvarez-Manzaneda, E. *Org. Lett.* **2016,** *18*, 5964-5967.

(32) Jadhav, A. N.; Kaur, N.; Bhutani, K. K. *Phytochem. Anal*. **2003**, *14*, 315-318.

(33) (a) Alvarez-Manzaneda, E.; Chahboun, R.; Cabrera, E.; Alvarez, E.; Haidour, A.; Ramos, J. M.; Alvarez-Manzaneda, R.; Hmamouchi, M.; Es-Samti, H. *Chem. Commun.* **2009**, 592-594. (b) Alvarez-Manzaneda, E.; Chahboun, R.; Alvarez, E.; Cano, M. J.; Haidour, A.; Alvarez-Manzaneda, R. *Org. Lett*. **2010,** *12*, 4450-4453.

(34) Lian, Y.; Miller, L. C.; Born, S.; Sarpong, R.; Davies, H. M. L. *J. Am. Chem. Soc.* **2010**, *132*, 12422-12425.

(35) The Diels-Alder cycloaddition of diene **17** and its 7-hydroxyderivative with DMAD, in the absence of solvent, to give the corresponding cycloadducts has been previously reported. See: Abad, A.; Agulló, C.; Castelblanque, L.; Cuñat, A. C.; Navarro, I.; Ramírez de Arellano, M. C. *J. Org. Chem.* **2000**, *65*, 4189-4192.

(36) A similar rearrangement has been previously described for some triterpene ketoacids. These compounds underwent decarboxylation with a methyl shift, in low yield, after heating to their melting points

(above 250 ºC). See: (a) Barnes, C. S.; Barton, D. H. R.; Fawcett, J. S.; Thomas, B. R. *J. Chem. Soc*. **1952**, 2339-2347. (b) Dauben, W. G.; Richards, J. H. *J. Am. Chem. Soc*. **1956**, *78*, 5329-5335.
(37) Li, H.-P.; Ai, H.-J.; Qi, X.; Peng, J.-B.; Wu, X.-F. *Org. Biomol. Chem.* **2017**, *15*, 1343-1345.
(38) Li, F. –Z.; Li, S.; Zhang, P.-P.; Huang, Z.-H.; Zhang, W.-B.; Gong, J.; Yang, Z. *Chem. Commun.* **2016**, *52*, 12426-12429.
(39) Pinto, A. C.; Antunes, O. A. C.; Rezende, C. M.; Correia, C. R. D. *Phytochemistry* **1995**, *38*, 1269-1271.