

## ARNOTTIANAMIDE AND OTHER CONSTITUENTS OF *ZANTHOXYLUM GILLETTII* ROOT<sup>1</sup>

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Previous chemical investigations (1,2) of *Zanthoxylum gillettii* Waterm. [syn. *Fagara macrophylla* (Planch ex. Oliv.) Engl., Rutaceae] describe the isolation of the furoquinoline alkaloid, skimmianine, the cinnamic acid amide, fagaramide, and the benzo [c] phenanthridine alkaloids, chelerythrine, dihydrochelerythrine, and nitidine. The present work describes the identification of arnottianamide, *N*-isobutyl-(2*E*,4*E*)-dodecadienamide, lupeol, *N*-isobutyl-2,4,8,10,12-tetradecapentaenamide ( $\gamma$ -sanshoöl), and sitosterol as new constituents. Arnottianamide isolated showed the same spectral data as a sample obtained on chemical modification of chelerythrine chloride.

This result represents a first detailed report of the identification of both aliphatic and aromatic amides in this plant. Sitosterol, lupeol,  $\gamma$ -sanshoöl, and fagaramide are known constituents of many Rutaceae species. *N*-isobutyl-(2*E*,4*E*)-dodecadienamide is a known constituent of *Piper peepuloides* (5) and has been found in trace amounts as a component of pellitorine obtained as the insecticidal fraction of *Anacyclus pyrethrum* roots (6). This is, however, its first report as a constituent of a Rutaceae species. Arnottianamide, now being reported for the first time in an African Rutaceae, has also been found in small amounts in *Fagara arborescens*, *Zanthoxylum arnottianum*, *Zanthoxylum bungeanum*,

and *Zanthoxylum cuspidatum* (7). Its facile preparation from chelerythrine chloride strongly supports the supposition (3) that it may have been formed through a similar Baeyer-Villiger-like oxidation process in vivo. Its occurrence with chelerythrine previously isolated from this plant bears some biogenetic significance.

### EXPERIMENTAL

**PLANT MATERIALS.**—The plant materials were collected fresh at a source near the Ile-Ife/Akure Road in Nigeria and were identified by Dr. O. A. Olatunji, Department of Botany, Obafemi Awolowo University, Ile-Ife, Nigeria. Voucher specimen (Olat. 595) was deposited at the Department of Botany Herbarium of the University. The plant material was dried at 45° in an aerated oven and powdered.

**EXTRACTION.**—The powdered material (540 gm) was extracted exhaustively with MeOH with three changes of solvent during 7 days. The MeOH extracts were pooled and reduced to a small volume to afford a thick yellow crude precipitate (473 mg, 0.088%) that was recovered by filtration and set aside. The filtrate was concentrated to dryness and treated with a 1:1 mixture of toluene and MeOH-H<sub>2</sub>O (2:1). The aqueous MeOH layer was further extracted with toluene (2 × 150 ml). The combined toluene extract was concentrated to a small volume to afford a sticky, gummy residue on the wall of the flask (fraction 1), and the supernatant was decanted (fraction 2).

**ISOLATION OF COMPOUNDS.**—Cc of fraction 2 over Si gel, on elution with hexane containing increasing amounts of EtOAc, gave  $\beta$ -sitosterol (7 mg, mp 137–139°, [M]<sup>+</sup> 414, 0.003%), lupeol (11 mg, mp 218–219°, [M]<sup>+</sup> 426, 0.002%), skimmianine (7 mg, mp 175–177°, [M]<sup>+</sup> 259, 0.003%), and arnottianamide (6 mg, mp 267–270°, [M]<sup>+</sup> 381, 0.0014%). Fraction 1 (ca. 103 mg, 0.019%) was dissolved in CHCl<sub>3</sub> and examined by gc-ms on SE 54 (4) and tlc [Si gel, CHCl<sub>3</sub>-toluene (1:1), CHCl<sub>3</sub>-MeOH

<sup>1</sup>Part 119 of "Natural Product Chemistry." For Part 118 see J. Reisch and A. Bathe, *Liebigs Ann. Chem.*, in press.

(190:10)] to reveal more than five compounds. Cc on a minor Si gel column eluted with hexane/EtOAc mixtures succeeded only partially in resolving this mixture. Repeated tlc chromatography and partial crystallization over long periods led to the isolation of small amounts of *N*-isobutyldodecatrans-2-*trans*-4-dienamide (7 mg, mp 93°,  $[M]^+$  251, 0.0013%), fagaramide (6.8 mg, mp 116–118°,  $[M]^+$  247, 0.0013%), and  $\gamma$ -sanshool (5 mg, mp 90°,  $[M]^+$  273, 0.0009%). The structure of arnottianamide was confirmed by a comparison of its spectral properties (uv, ir, ms), mp, and chromatographic behavior with that of a specimen obtained by the treatment of chelerythrine chloride with *m*-chloroperbenzoic acid in hexamethylphosphorotriamide at 38–40° (3). It also furnished the monoacetate (pyridine/Ac<sub>2</sub>O), mp 237–238°; ms *m/z* (rel. int.); 423 (18),  $[M-42]^+$  381 (64), 353 (26), 322 (66), 307 (34), 179 (24), 135 (49), 69 (58), 57 (100) for C<sub>23</sub>H<sub>21</sub>NO<sub>7</sub>.

Further details of our methods and analytical data are available on request as indicated.

#### ACKNOWLEDGMENTS

We thank Dr. Olarunji and Mr. Doye Akin-

wusi, Obafemi Awolowo University, Ile-Ife, for botanical help. S.K.A. thanks the Deutsch Akademischer Austauschdienst (DAAD) for a fellowship. This research was also supported financially by the Deutsche Forschungsgemeinschaft and Obafemi Awolowo University (Research Grant No. 1425 LV to S.K.A.).

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Received 17 November 1987