

DITERPENOIDS FROM *PALAFoxia ROSEA*

XORGE A. DOMÍNGUEZ, CARMEN CISNEROS, ELSA GUAJARDO T., ROMELIA VILLARREAL and ANGELES ZAMUDIO

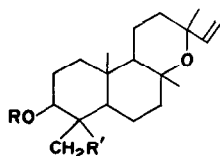
Departamento de Química, Instituto Tecnológico y de Estudios Superiores de Monterrey, Monterrey, N.L. México

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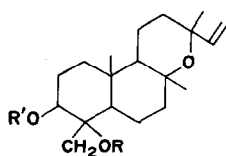
**Key Word Index**—*Palafoxia rosea*; Compositae; diterpenoids; 18-deoxylazarcardenasol (3-hydroxymanoyl oxide); 18-benzoxylazarcardenasol (18-benzoxy-3-hydroxymanoyl oxide).

**Plant:** *Palafoxia rosea* (Bush) Compositae **Source:** Tampico, Tamps. August 1973, Voucher specimen 7296. **Previous work.** None on this or sister species [1].

**Present work.** Besides the common sitosterol, we have isolated 18-deoxylazarcardenasol ( $\beta$ -hydroxymanoyl oxide), (1) and 18-benzoxylazarcardenasol (18-benzoxy-3-hydroxymanoyl oxide) (2). Direct  $\text{CHCl}_3$  and EtOH extracts were investigated [2] unsuccessfully for sesquiterpene lactones, alkaloids and cardenolides.



(1a)  $R = H$ ;  $R' = H$   
(1b)  $R = \text{MeCO}$ ;  $R' = H$



(2)  $R = \text{C}_6\text{H}_5\text{CO}$ ;  $R' = H$   
(3)  $R' = H$ ;  $R = H$

The aerial part was dried, powdered and 2.8 kg were extracted with petrol. Each extract was chromatographed on Si gel. On elution with solvents of increasing polarity, the petrol concentrate (60 g), afforded 280 mg of sitosterol, mmp ( $\alpha$ ), IR, coTLC; acetate, mmp, ( $\alpha$ ) coTLC; 1.6 g of 18-deoxylazarcardenasol (3-hydroxymanoyl oxide) (1a)  $\text{C}_{20}\text{H}_{34}\text{O}_2$  ( $M^+$  306), mp 85–87°, ( $\alpha$ ),  $\frac{22}{589}$  –34.8°; ( $\alpha$ )  $\frac{576}{576}$  –35.6°, ( $\alpha$ )  $\frac{546}{546}$  –39.1°, ( $\alpha$ )  $\frac{436}{436}$  –69.7°, ( $\alpha$ )  $\frac{365}{365}$  –111.4°, ( $\alpha$ )  $\frac{316}{316}$  –176.9° (Chl), UV,  $\lambda_{\text{max}}^{\text{H}_2\text{O}}$  197 nm (1128), IR: (KBr)  $\nu$  3450, 1610, 1160, 1190, 900, 830  $\text{cm}^{-1}$ ; NMR: ( $\text{CDCl}_3$ )  $\delta$  6.3–5.8 (1H *m*,  $\text{CH}_2=\text{CH}-$ ), 5.1 (1H, *d*,  $\text{CH}_2=\text{CH}-$ ), 4.85 (1H, *d*,  $\text{CH}_2=\text{CH}$ ), 2.3–1.3 (18H, *m*), 1.20 (3H, *s*), 1.11 (3H, *s*), 0.99 (3H, *s*), 0.80 (3H, *s*). ME: *m/e* (abundance)  $M^+$  306 (1), 291 (100), 273 (18),

255 (42), 207 (20), 190 (35), 175 (22), 161 (10), 147 (18), 135 (58), 121 (35), 107 (37), 95 (50), 81 (85), 67 (65), 55 (90), 43 (100).

18-Deoxylazarcardenasol acetate (1b),  $\text{C}_{22}\text{H}_{36}\text{O}_3$  ( $M^+$  348), mp 147°; ( $\alpha$ )  $\frac{24}{589}$  –52.3°; ( $\alpha$ )  $\frac{578}{578}$  –52.5°; ( $\alpha$ )  $\frac{546}{546}$  –60.3°; ( $\alpha$ )  $\frac{436}{436}$  –101°; ( $\alpha$ )  $\frac{365}{365}$  –160.6°; ( $\alpha$ )  $\frac{316}{316}$  –247.2°; (Chl). IR,  $\text{KBr}^-$  1725, 1610, 1250  $\text{cm}^{-1}$ ; NMR, 2.0 (3H, *s*). 18-deoxylazarcardenasone  $\text{C}_{20}\text{H}_{32}\text{O}_2$ , ( $M^+$  304), mp 115° ( $\alpha$ )  $\frac{22}{589}$  –71°; ( $\alpha$ )  $\frac{578}{578}$  –76.1°; ( $\alpha$ )  $\frac{546}{546}$  –85.7°; ( $\alpha$ )  $\frac{436}{436}$  –157.9°; ( $\alpha$ )  $\frac{365}{365}$  –277.5°; ( $\alpha$ )  $\frac{316}{316}$  –279° (Chl). IR, 1700, 1600  $\text{cm}^{-1}$ ; NMR  $\delta$  6.3–5.8 (1H, *m*), 5.15 (1H, *d*), 4.85 (1H, *d*), 2.52 (2H, *t*), 1.30 (3H, *s*), 1.15 (3H, *s*), 1.05 (3H, *s*), 0.85 (3H, *s*). 18-deoxylazarcardenasone on Wolff-Kishner reduction gave manoyl oxide, IR, coTLC with an authentic sample. 18-deoxydihydrolazarcardenasol. Hydrogenation of (1a) in presence of 10% Pd-C Small crystals, mp 90°,  $\text{C}_{20}\text{H}_{36}\text{O}_2$ . ( $\alpha$ )  $\frac{589}{589}$  –20°, ( $\alpha$ )  $\frac{578}{578}$  –20.4°; ( $\alpha$ )  $\frac{546}{546}$  –23.2°; ( $\alpha$ )  $\frac{436}{436}$  –40.4°; ( $\alpha$ )  $\frac{365}{365}$  –66°, NMR, multiple signals at 1.8–0.85 (32H). UV, no absorb. IR,  $\bar{\nu}$ , KBr, 3450, 2900, 1430, 1350, 1160, 930  $\text{cm}^{-1}$  of 18-benzoxylazarcardenasol (550 mg) (2), mp 195°,  $\text{C}_{27}\text{H}_{38}\text{O}_4$ ; [ $\alpha$ ] $\frac{22}{589}$  –28.7°; ( $\alpha$ )  $\frac{578}{578}$  –29.0°; ( $\alpha$ )  $\frac{546}{546}$  –32.5°; ( $\alpha$ )  $\frac{436}{436}$  –56.2°; ( $\alpha$ )  $\frac{365}{365}$  –87.4°; ( $\alpha$ )  $\frac{316}{316}$  –91.4° (Chl). UV,  $\lambda_{\text{max}}^{\text{H}_2\text{O}}$  202 nm ( $\epsilon$  15054), 228 nm ( $\epsilon$  36514), 270 nm ( $\epsilon$  6391), 280 nm ( $\epsilon$  3203). IR, 3500 (OH), 2900 (Me,  $\text{CH}_2$ ), 1700 (CO), 1650, 1600, 1500, 1425, 1350, 1255, 1220, 1042, 934, 905, 833, 714  $\text{cm}^{-1}$ . NMR  $\delta$  8.0 (2H, *m*), 7.5 (3H, *m*), 6.3–5.8 (1H, *m*), 5.3–4.8 (2H, *m*), 3.5–3.3 (2H, *d*) 2.5 (2H), 1.3 (3H, *s*), 1.15 (3H, *s*), 0.85 (3H, *s*), 0.80 (3H, *s*), lazarcardenasdiol-3,18 (3), the ester 2 on KOH-MeOH hydrolysis gave 3, mp 167°,  $\text{C}_{20}\text{H}_{34}\text{O}_3$ . ( $\alpha$ )  $\frac{24}{589}$  –35.5°; ( $\alpha$ )  $\frac{578}{578}$  –37.1°; ( $\alpha$ )  $\frac{546}{546}$  –38.8°; ( $\alpha$ )  $\frac{436}{436}$  –70.4°; ( $\alpha$ )  $\frac{365}{365}$

—117.5°; ( $\alpha$ )<sub>316</sub> —191.5°. IR,  $\bar{\nu}$  3450, 2900, 1620, 1450, 1362, 1075, 1064, 1042, 1020, 998, 917, 833  $\text{cm}^{-1}$ . NMR,  $\delta$  6.3–5.8 (1H, *dd*), 5.3–4.8 (2H, *m*), 3.8–3.3 (2H, *dd*), 1.25 (3H, *s*), 1.15 (3H, *s*), 0.9 (3H, *s*), 0.85 (3H, *s*).

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### $\alpha$ - AND $\beta$ -AMYRIN ESTERS AND SITOSTEROL GLUCOSIDE FROM *SPILANTHES ACMELLA*

N. R. KRISHNASWAMY and S. PRASANNA

Department of Chemistry, Bangalore University, Central College, Bangalore 560001, India

and

T. R. SESHADRI and T. N. C. VEDANTHAM\*

Department of Chemistry, University of Delhi, Delhi 110007, India

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**Key Word Index**—*Spilanthes acmella*; Compositae; fatty acid esters of  $\alpha$ - and  $\beta$ -amyrins; myricyl alcohol; stigmasterol; sitosterol-*O*- $\beta$ -D-glucoside.

**Plant.** *Spilanthes acmella* Linn. (Voucher specimen No. C-1/73, deposited at the Department of Botany, Bangalore University.) **Uses.** Medicinal [1, 2]. **Previous work.** Spilanthol [3–5]; on sister species [6–8]. **Present work.** Air-dried whole plant of *S. acmella* was extracted with light petrol, followed by 90% EtOH. The light petrol extract when subjected to adsorption chromatography over neutral  $\text{Al}_2\text{O}_3$  yielded the following fractions: (a) A viscous semi-solid (light petrol eluate), homogeneous on TLC; IR spectrum showed ester CO. Hydrolysis with methanolic alkali yielded a mixture of  $\alpha$ - and  $\beta$ -amyrins, separated and identified as their acetates. Methanolysis of the parent ester with methanolic HCl followed by GLC, showed lauric, myristic, palmitic (major component), linoleic and linolenic acids as their methyl esters. (b) Mixture of  $\alpha$ - and  $\beta$ -amyrin acetates (light petrol- $\text{C}_6\text{H}_6$ , 4:1), separated by repeated fractional crystallization from

MeOH and subsequently from  $\text{CHCl}_3$ - $\text{Et}_2\text{O}$ ; identities confirmed by direct comparison with authentic samples (mp, mmp,  $[\alpha]_D$  and IR.) (c) Myricyl alcohol (light petrol- $\text{C}_6\text{H}_6$ , 2:1 eluates), mp 85–86°, acetyl derivative, mp 71–72° on direct comparison with authentic samples. (d) Mixture of  $\alpha$ - and  $\beta$ -amyrins (light petrol- $\text{C}_6\text{H}_6$ , 1:1 eluates) separated and identified through their acetates and (e) Stigmasterol (light petrol- $\text{C}_6\text{H}_6$ , 1:2 eluates), mp, mmp, acetyl, co-TLC.

The ether extract of the alcoholic concentrate gave an amorphous green solid which was purified by adsorption chromatography over Si gel ( $\text{CHCl}_3$ -MeOH, 92:8 eluates) and subsequent crystallization from dioxan to yield sitosterol-*O*- $\beta$ -D-glucoside, mp 304–306°; tetra acetate, mp 168–170°,  $[\alpha]_D^{25}$  —31.6° ( $\text{CHCl}_3$ ). It was hydrolysed to sitosterol and D-glucose. The identities of the glucoside and its acetate were confirmed by direct comparison with authentic samples (mp, co-TLC, NMR [9], IR).

\* Present address: Department of Chemistry, JIPMER, Pondicherry 605006, India.