

Note

Disubstituted tetrahydrofuran and an ester from *Argyrea speciosa*[†]

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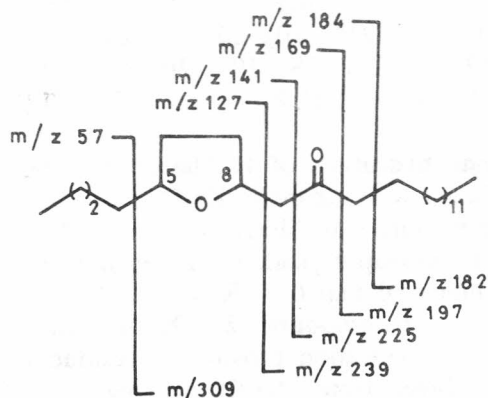
Received 16 July 1996; revised and accepted 4 November 1996

Two new compounds isolated from the roots of *Argyrea speciosa* have been characterized as tetradecanoyl palmitate **1** and 5,8-oxidotetracosan-10-one **2** by physico-chemical evidence.

Argyrea speciosa (Convolvulaceae), commonly known as Elephant Creeper is a woody climber distributed¹ throughout India upto an altitude of 300 m. The seeds are rich source of ergoline alkaloids while the roots are reported^{1,2} to be tonic, bitter, aphrodisiac, diuretic and used in rheumatism, gonorrhoea, chronic ulcer and diseases of nervous system. Since no work has been reported on roots a systematic investigation on the root extract was initiated. The characterization of two constituents, tetradecanoyl palmitate **1** and 5,8-oxidotetracosan-10-one **2** is reported herein.

Chromatography of the hexane fraction over silica gel yielded compounds **1** and **2**. Compound **1** [IR: 2920, 2850, 1450, 725, 720 (straight chain), 1380 (CH₃), 1736 and 1250 cm⁻¹ (ester CO)] had in its ¹H NMR spectrum two triplets (*J* = 6 Hz) at δ 2.24 and 4.0 for -COCH₂ and -CH₂-O-CO- functions, respectively. Alkaline hydrolysis of **1** afforded palmitic acid (m.p., IR, mass spectrum) and tetradecanol (IR, MS). This compound was therefore characterized as tetradecanoyl palmitate.

The IR spectrum of compound **2** showed bands for CO (1740 cm⁻¹), -C-O-C (1240 cm⁻¹), and straight-chain functions. An [M]⁺ at *m/z* 366 in its mass spectrum was in agreement with the molecular formula C₂₄H₄₆O₂. Prominent α-fission ions at *m/z* 225, 197, 169 and 41 together with the β-fission ions involving McLafferty rearrangement³ at *m/z* 184 and 182 established the location of CO group at C-10 in the molecule. The strong ions at *m/z* 68 [C₄H₄O]⁺, 69 and 70 [C₄H₆O]⁺ were due to the presence of a tetrahydrofuran ring in the compound^{4,5}. The location of



Scheme I - Mass spectral fragmentation of **2**.

the ring between C-4 and C-9 was evident from the ions at *m/z* 309, 57, 239 and 127 (Scheme I). The ¹H NMR spectrum of this compound was also consistent with its structure as **2** (see Experimental).

Straight-chain epoxy, polyhydroxy and furanoid compounds^{6,7} are known to occur widely in nature but disubstituted tetrahydrofuran with a CO group in the chain are rare⁸.

Experimental Section

Melting points are uncorrected. The IR spectra were recorded in KBr and the 80 MHz ¹H NMR spectra in CDCl₃ with the TMS as internal standard. TLC analyses were carried out on silica gel plates and the spots were visualized by exposure to I₂ vapours. The roots were collected from local area and identified in our Botany Department, where a voucher specimen is maintained.

Isolation of compound 1. The air-dried and powdered roots (1.6 kg) were extracted with MeOH (10 × 4.5 L), the combined extracts concentrated to 500 mL and water (500 mL) was added to it. The aq. methanolic extract was then fractionated successively with *n*-hexane (5 × 1 L), EtOAc (5 × 11) and *n*-BuOH (5 × 500 mL). Removal of solvent from the hexane extract yielded a residue (45 g), a portion of which (22 g) was chromatographed over silica gel (600 g). Elution was carried out with hexane, hexane-C₆H₆, C₆H₆, C₆H₆-CHCl₃, CHCl₃ and CHCl₃-MeOH. Fractions (100 mL each) were collected and monitored by TLC. The residue from hexane-C₆H₆ fractions yielded a solid, crystallized from CHCl₃-

[†]CIMAP Publication No. 96-28J

MeOH (70 mg), m.p. 76°; IR: 2920, 2850, 1736, 1450, 1380, 1250, 725, 720 cm^{-1} ; $^1\text{H NMR}$: δ 0.88 (6H, t, $J=6$ Hz, 2x terminal Me), 1.25 [50H, brs, $(\text{CH}_2)_{25}$], 2.24 (2H, t, $J=6$ Hz, $-\text{CH}_2-\text{CO}-$), 4.0 (2H, t, $J=6$ Hz, $-\text{CH}_2-\text{O}-\text{CO}-$); MS m/z (rel. int): 452 $[\text{M}]^+$ ($\text{C}_{30}\text{H}_{60}\text{O}_2$) (1), 256 (10), 255 (8), 241 (11), 239 (15), 213 (16), 211 (18), 197 (20), 196 (15), 127 (15), 113 (20), 99 (25), 85 (40), 71 (50), 57 (100), 43 (70).

Alkaline hydrolysis of 1. The ester **1** (60 mg) was refluxed with ethanolic KOH (5%, 20 mL, 5 hr). The mixture was diluted with water (100 mL) and after work-up it yielded tetradecanol (IR, MS) and palmitic acid, m.p. 65° (IR, MS).

Isolation of compound 2. The benzene fractions on concentration provided a residue which was crystallized from MeOH, (30 mg), m.p. 65°; IR: 2920, 2850, 1740, 1450, 1380, 1240, 725, 715 cm^{-1} ; $^1\text{H NMR}$: δ 0.88 (6H, t, $J=6$ Hz, 2x terminal Me), 1.50 (2H, m, H_2-4), 4.14 (2H, m, H_2-5 , H_2-8), 1.95 (4H, m, H_2-6 , H_2-7), 2.35 (2H, d, $J=7$ Hz, H_2-9), 2.24 (2H, t, $J=6$ Hz, H_2-11), 1.25 (28H, brs, $14 \times \text{CH}_2$); MS m/z (rel int): 366 $[\text{M}]^+$ ($\text{C}_{24}\text{H}_{46}\text{O}_2$) (4), 323 (3), 309 (15), 239 (20), 225 (10), 197 (100), 184 (25), 182 (10), 169 (21),

141 (25), 127 (13), 70 (18), 69 (15), 68 (20), 57 (20), 43 (60).

Acknowledgement

The authors are grateful to Dr Sushil Kumar, Director, CIMAP, Lucknow for his encouragements during the course of this work.

References

- 1 *The Wealth of India—Raw Materials*, (PID, New Delhi), 1985, p. 418.
- 2 Chopra R N, Nayar S L & Chopra I C, *Glossary of Indian Medicinal Plants*, (CSIR, New Delhi, 1956, p. 24.
- 3 Budzikiewicz H, Djerassi G & Williams D H, *Interpretation of Mass Spectra of Organic Compounds*, (Holden-Day, San Francisco), 1965, p. 6.
- 4 Bhakuni R S, Shukla Y N & Thakur R S, *Phytochemistry*, 26, 1987, 2607.
- 5 Tandon M, Shukla Y N & Thakur R S, *Phytochemistry*, 31, 1992, 2525.
- 6 Gunstone F D, in *Comprehensive Organic Chemistry*, Vol 5, edited by E Haslam (Pergamon Press, Oxford), 1979, p. 595.
- 7 Devon T K & Scott A I, *Handbook of Naturally Occurring Compounds*, Vol. 1, (Academic Press, New York), 1975, p. 498.
- 8 Zeng L, Ye Q, Oberlies N H, Shi G, Gu Z-M, He K & McLaughlin J L, *Nat Prod Rep*, 13, 1996, 275.