

Aliphatics and triterpenoids from the heartwood of *Dichrostachys cinerea*

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Chemical investigation of combined pet. ether and benzene solubles from the ethanolic extract of *Dichrostachys cinerea* (heartwood) afforded a new hydroxy ester, 6-hydroxypentacosyl pentanoate along with α -amyrin palmitate, *n*-triacontane, 1-octyl docosonoate, ceryl cerotate, friedelin, stigmastanol, epifriedelinol, α -amyrin, γ -sitosterol, β -sitosterol and lacceric acid.

Dichrostachys cinerea Wight & Arn. syn. *Cailliea cinerea* Mach. (Family : Mimosaceae) is a small tree, occurring in the dry scrub forests and arid zone of India. It serves as a host-plant for lac insects, while the tender shoots are used in ophthalmia. The root is astringent, cures rheumatism, strangury, urinary calculi and renal troubles, diseases of the vagina, uterus and joint pain¹. A survey of literature revealed the isolation of several triterpenoids, aliphatic alcohols and sterols from its leaves, stem bark, roots and pods^{2,3}. Since systemic investigation of the heartwood is lacking, except the isolation of β -sitosterol and octacosanol³, hence the present investigation was undertaken.

The heartwood of plant was collected from the Rajasthan University Campus, Jaipur, and identified from the Department of Botany, University of Rajasthan, Jaipur (Herbarium sheet no. RUBL 19763). It was air-dried (5 kg), powdered and exhaustively extracted with ethanol (95%) on a steam-bath for 8 $\times$ 3 h. The extract was concentrated under reduced pressure when a dark brown semi-solid (130 g) was obtained. The ethanolic extract was fractionated into pet. ether and benzene solubles resulting into yellowish brown (10.2 g) and brown (7.8 g) concentrates, respectively. On TLC examination (C_6H_6 : EtOAc, 1 : 1), both the fractions exhibited a similar pattern hence these were mixed and chromatographed over silica gel which on elution with solvents of increasing polarity afforded twelve crystalline compounds.

α -Amyrin palmitate : Elution with pet. ether afforded a colourless waxy solid (240 mg) which was crystallized as white microcrystals ($CHCl_3$: MeOH), m.p. 71–72°, $C_{46}O_{80}O_2$ (M^+ 664). Hydrolysis (alc. KOH) afforded white needles of α -amyrin, m.p. 183–184°, $C_{30}H_{50}O$ (M^+ 426), confirmed by comparative spectral data and preparation of acetate, m.p. 221–223° and its hydrolyzate furnished white microneedles (EtOAc) of palmitic acid, m.p. 59–60°, $C_{16}H_{32}O_2$ (M^+ 256).

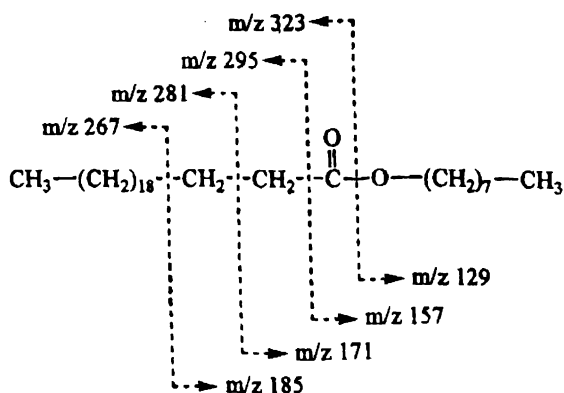
n-Triacontane : Elution with pet. ether afforded a white solid (227 mg) which was crystallized as a white amorphous powder ($CHCl_3$: MeOH), m.p. 64°, $C_{30}H_{62}$ (M^+ 422).

1-Octyl docosonoate : Elution with pet. ether afforded a pale yellow solid (294 mg) which was crystallized as colourless crystals, m.p. 91–93°, $C_{30}H_{60}O_2$. It exhibited IR peaks at 1740 (saturated ester), 1240 ($C_{sp^2}-O$), 1040 ($C_{sp^3}-O$) and the doublet at 740 and 730 cm^{-1} (long carbon chain). Its ^1H NMR spectrum displayed signals at δ 0.88 (t, 2 $\times$ CH_3), 1.24 (br t, 25 $-CH_2-$), 2.28 (t, CH_2-CO) and 4.05 (t, CH_2-O-CO). Its mass spectrum showed molecular ion peak at m/z 452 (M^+) and other significant peaks at m/z 409, 323, 295, 185, 171, 157 and 129 together with many peaks with uniform loss of 14 mass units which could be explained in terms of structure **1** for the compound (Scheme 1)⁴.

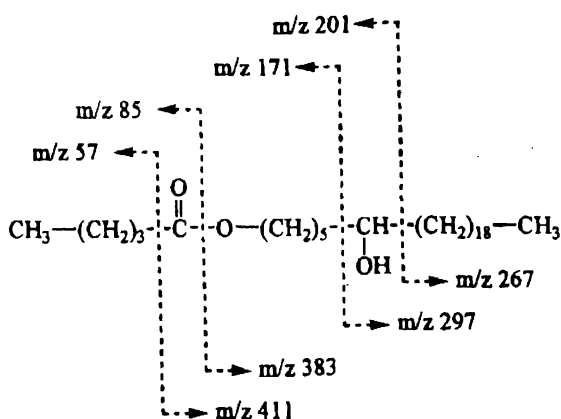
Ceryl cerotate : Elution of column with pet. ether afforded a colourless waxy solid (268 mg) which afforded white crystals (EtOAc), m.p. 82–83°. Hydrolysis with ethanolic KOH afforded white crystals of ceryl alcohol, m.p. 77–78°, M^+ 382, confirmed by preparation of its acetate, m.p. 63–64°, and the acid moiety obtained as a white solid, m.p. 85–86°, M^+ 396, was identified as cerotic acid, confirmed by the preparation of its methyl ester, m.p. 60–61°.

Friedelin : It was eluted with pet ether : benzene (3 : 1) as a white solid (116 mg) which was crystallized as white microneedles, m.p. 258–60°², $C_{30}H_{50}O$ (M^+ 426) and confirmed by preparation of its oxime, m.p. 290–92° and co-IR with an authentic sample.

Fractions obtained on elution with pet. ether : benzene (3 : 2) appeared to be a mixture of two compounds (TLC) hence they were rechromatographed over silica gel when elution with pet. ether : benzene (9 : 1) and (4 : 1) afforded stigmastanol and epifriedelinol, respectively.



(1)



(2)

Scheme 1

Stigmastanol : It was obtained as a yellow solid (225 mg) which was crystallized as white needles (MeOH), m.p. 145–147°, $\text{C}_{29}\text{H}_{52}\text{O}$ (M^+ 416), confirmed by preparation of its acetate ($\text{Ac}_2\text{O/Py}$), m.p. 132–133°.

Epifriedelinol : It was eluted as a white solid (240 mg) and crystallized as white needles (acetone), m.p. 277–278°, $\text{C}_{30}\text{H}_{52}\text{O}$ (M^+ 428), acetate ($\text{Ac}_2\text{O/Py}$), m.p. 291–294°, and finally confirmed by comparison with an authentic sample.

α -Amyrin : It was eluted with pet. ether : benzene (2 : 3) as a colourless solid (309 mg) which was purified by repeated crystallization as white needles (CHCl_3 : MeOH), m.p. 183–184°, $\text{C}_{30}\text{H}_{50}\text{O}$ (M^+ 426), acetate ($\text{Ac}_2\text{O/Py}$), m.p. 222–223° and benzoate, m.p. 193°.

γ -Sitosterol : Elution with pet. ether : benzene (1 : 4) afforded a yellowish white solid (153 mg) which on crystallization afforded a colourless solid (CHCl_3 : MeOH),

m.p. 146–147°, $\text{C}_{29}\text{H}_{50}\text{O}$ (M^+ 414), confirmed by preparation of its acetate ($\text{Ac}_2\text{O/Py}$), m.p. 142° and benzoate, m.p. 150°.

β -Sitosterol : Further elution with pet. ether : benzene (1 : 4) afforded a white solid (268 mg) which was crystallized as white needles (CHCl_3 : MeOH), m.p. 135–136°, $\text{C}_{29}\text{H}_{50}\text{O}$ (M^+ 414) confirmed by co-TLC with authentic sample.

Lacceric acid : Elution with pet. ether : benzene (1 : 4) further afforded a white waxy solid (112 mg) which was crystallized as a white microcrystalline powder (CHCl_3 : MeOH), m.p. 79–84°, $\text{C}_{32}\text{H}_{64}\text{O}_2$ (M^+ 480), confirmed by preparation of its methyl ester, m.p. 54–56°.

6-Hydroxypentacosyl pentanoate : Elution with benzene : EtOAc (4 : 1) afforded a white residue (310 mg), crystallized as a white amorphous powder (CHCl_3 : MeOH), m.p. 83–84°, $\text{C}_{30}\text{H}_{60}\text{O}_3$. Its IR spectrum showed absorptions at 3390 (O–H), 1730 (C=O), 1135 (O=C–O) and 1080 cm^{-1} (C–OH). Its ^1H NMR spectrum displayed signals for the presence of two methyl groups at δ 0.81 (6H, t), 24 methylene groups at 1.18 (48H, t) and a methine proton geminal to hydroxyl group at 3.55 (1H, m). Two proton triplets appearing at δ 4.11 and 2.24 corresponded to $-\text{CH}_2-$ group attached to ester oxygen and carbonyl, respectively. In its mass spectrum, molecular ion peak appeared at m/z 468 (M^+) and other significant peaks at m/z 411, 383, 297, 267, 201, 171, 85 and 57 together with many peaks with uniform loss of 14 mass units (Scheme 1). The straight-chain nature was confirmed by the absence of an (M^+ –15) ion⁵, whereas the presence of a peak at m/z 469 corresponding to ($M+1$)⁺ ion was characteristic of its asymmetrical nature⁶. All the foregoing evidences led to the characterization of compound as 6-hydroxypentacosyl pentanoate (2), being reported for the first time from nature.

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References

1. K. R. Kiritkar and B.D. Basu, "Indian Medicinal Plants", Lalit Mohan Basu and Co., Allahabad, 1975, Vol II, p. 912; R. N. Chopra, S. L. Nayar and I. C. Chopra, "Glossary of Indian Medicinal Plants", C.S.I.R., New Delhi, 1971, p. 191.
2. K. C. Joshi and T. Sharma, *Phytochemistry*, 1974, **13**, 2010.
3. H. P. S. Makkar and K. Recker, *J. Agric. Food Chem.*, 1994, **42**, 731; A. M. Khattab, *Bull. Fac. Pharm.*, 1998, **36**, 53; K. C.

- Joshi and T. Sharma, *J. Indian Chem. Soc.*, 1977, **54**, 649; J. V. Standen, K. M. Kelly and W. E. Bell, *Plant Growth Regul.*, 1994, **14**, 273; V. Krishnamoorthy and T. R. Seshadri, *J. Sci. Ind. Res., Sect. B*, 1963, **21**, 591.
4. R. Ryhag and E. Stenhagen in "Mass Spectrometry of Organic Ions", ed. F. W. McLafferty, Academic, New York, 1963; H. Budzikiewicz, C. Djerassi and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds", Holden Day, San Francisco, 1965.
5. I. B. Stoianova and P. Hadjieva, *Phytochemistry*, 1969, **8**, 1549.
6. J. H. Beynon, G. R. Laster, R. A. Saunders and A. E. Williams, *Trans. Faraday Soc.*, 1961, **57**, 1259; D. Chakravarti and N. B. Debnath, *J. Indian Chem. Soc.*, 1974, **51**, 260.