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Flavonoids of *Derris heyneana* wight and arm

S. Ganapaty [a]*, C. H. Bharath [a], P. Steve Thomas [a], S. Fotso [b], H. Laatsch [b]

a. Pharmacognosy and Phytochemistry Division, Department of Pharmaceutical Sciences, Andhra University, Visakhapatnam - 530 003, Andhra Pradesh, India

b. Institute for Organic and Biomolecular Chemistry, Georg - August University, Göttingen, Tammannstrasse 2 D - 37077 Göttingen.

Abstract

The genus *Derris* is a rich source of rotenoids and prenylated flavonoids. Chemical examination of *Derris heyneana*, a rare species of *Derris*, led to the isolation of stigmasterol, lupeol, three rotenoids, 6a,12a-dehydrotoxicarol, dehydrodeguelin, 12-deoxo-12α-acetoxyelliptone and the isoflavone, 4-O-methylderrone. All compounds were isolated by sequential chromatography and characterized by NMR and MS spectral data. The flavonoids are reported for the first time from *D. heyneana*.

Key words: *Derris heyneana*, Fabaceae, flavonoids.

1. Introduction

Derris heyneana Wight and Arm is a spreading and climbing shrub, distributed throughout the plains of Southeast Asia. The roots are used as an insecticidal, larvicidal, expectorant, antitussive, diuretic, antimicrobial, anti-fertility and for cancer chemopreventive remedy [1-3]. Earlier, we have reported the isolation of a new chalcone (Hyeneanachalcone A) and three C-prenylflavonoids from the leaves of *D. heyneana* [4]. In continuation of our studies on Derris, we report here, the isolation and structure determination of three rotenoids, 6a,12a dehydrotoxicarol, 12-deoxo-12α-acetoxyelliptone, dehydrodeguelin and an isoflavone, 4-O-methylderrone from the roots of this species. These flavonoids are reported for the first time from *D. heyneana*.

2. Materials and methods

2.1 Plant material

The roots of *Derris heyneana* were collected from Amboli ghat, Konkan coast of Maharastra, India and were authenticated by Dr. P.S.N. Rao, Joint Director, Botanical Survey of India, Western Circle-7, Pune, India. A voucher specimen (SG / DHR / 04 / 339) has been deposited at the herbarium, Department of Pharmaceutical Sciences, Andhra University, Visakhapatnam, India.

* Corresponding author
Email: ganapatyseru@gmail.com

2.2 Extraction

The air dried roots (1.5 kg) of *D. heyneana* were powdered and extracted with chloroform (3 L each) for four times and the extracts were combined and concentrated under reduced pressure to get a reddish brown residue (180 g). The extract gave a positive Liebermann-Burchard reaction for sterols and triterpenoids and positive test for phenolic compounds with ferric chloride.

2.3 Isolation and characterization of the compounds

A portion of the chloroform extract (150 g) was column chromatographed over silica gel (Acme, 100-200 mesh) using petroleum ether, petroleum ether-chloroform, chloroform, and chloroform-methanol mixtures as eluents. Six compounds were isolated and purified by a series of chromatographic techniques. They were identified as 4-O-methyl derrone **(1)**, stigmasterol **(2)**, 6a,12a-dehydrotoxicarol **(3a)**, dehydrodoguelin **(3b)**, lupeol **(4)** and 12-deoxo-12α-acetoxyelliptone **(5)**. The isolates were characterized by ^{1}H NMR, ^{13}C NMR, HMQC and HMBC experiments.

2.4. Experimental

4'-O-Methylderrone [5] **(1)**: Yellow needles, m.p. 168-170 °C, ^{1}H NMR ($CDCl_3$) δ: 13.16 (1H, s, 5-OH), 7.82 (1H, s, H-2), 7.42 (2H, *d*, *J* = 9 Hz, H-2'/6'), 6.97 (2H, *d*, *J* = 9 Hz, H-3'/5'), 6.72 (1H, *dd*, *J* = 10 Hz, H-4"), 6.34 (1H, *d*, *J* = 0.7 Hz, H-6), 5.62 (1H, *d*, *J* = 10 Hz, H-3"), 3.84 (3H, s, OMe), 1.47 (6H, s, Me-2"), ^{13}C NMR ($CDCl_3$): 180.9 (C-4), 159.6 (C-5), 159.9 (C-8a), 157.4 (C-7), 157.1 (C-4'), 152.4 (C-2), 130.2 (C-2',6'), 128.1 (C-3"), 123.6 (C-1'), 123.2 (C-3), 115.6 (C-4"), 114.2 (C-3',5'), 106.2 (C-4a), 105.6 (C-8), 94.9 (C-6), 78.1 (C-2"), 55.4 (OMe), 28.3 (Me_2). EIMS *m/z* (%): 350 ([M]$^{+}$, 22), 335 (100), 203 (7), 167 (18), 132 (5).

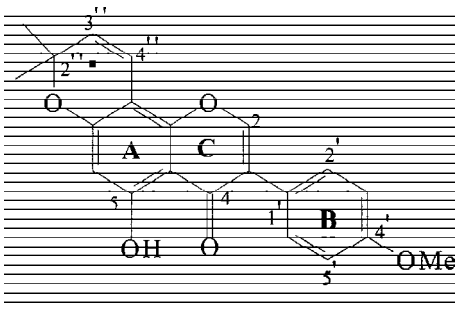
Stigmasterol **(2)**: Colourless needles. ^{1}H NMR identical with those of authentic 3ß-stigmast-5-en-3-ol. EIMS: *m/z*: 414 (M^{+}) [6].

6a,12a-Dehydrotoxicarol (6-Hydroxy-9,10-dimethoxy-3,3-dimethyl-3H,13H-pyrano[2,3-c;6,5-f']dichromen-7-one) [7] **(3a)**: ^{1}H NMR ($CDCl_3$) δ: 12.99 (1H, *s*, OH), 8.28 (1H, *s*, H-1), 6.64 (1H, *d*, *J* = 10.0 Hz, H-4'), 6.57 (1H, *s*, H-4), 6.30 (1H, *s*, H-10), 5.59 (1H, *d*, *J* = 10.0 Hz, H-3'), 5.01 (2H, *s*, CH_2-6), 3.88, 3.94 (each 3H, 2*s*, 2/3-OMe), 1.47 (6H, *s*, 2'-Me_2).

Dehydrodeguelin (9,10-Dimethoxy-3,3-dimethyl-3H,13H-pyrano[2,3-c;6,5-f']dichromen-7-one) [10] **(3b)**: Yellow crystalline compound. ^{1}H NMR ($CDCl_3$) δ: 8.46 (1H, *br s*, H-1), 8.06 (1H, *d*, *J* = 8.7 Hz, H-11), 6.86 (1H, *d*, *J* = 8.7 Hz, H-10), 6.77 (1H, *d*, *J* = 10.0 Hz, H-4'), 6.56 (1H, *br s*, H-4), 5.74 (1H, *d*, *J* = 10.0 Hz, H-3'), 5.02 (2H, *s*, H2-6), 3.96 (3H, *s*, 3-OMe), 3.87 (3H, *s*, 2-OMe), 1.52 (6H, *s*, 2'-Me_2). ^{13}C NMR ($CDCl_3$) δ: 174.1 (C-12), 157.2 (C-9), 156.0 (C-6a), 151.1 (C-7), 149.2 (C-3), 146.3 (C-4a), 144.1 (C-2), 130.5 (C-11), 126.5 (C-3'), 118.5 (C-11a), 115.3 (C-4'), 114.7 (C-10), 111.8 (C-12a), 110.5 (C-8), 110.4 (C-1), 109.2 (C-1a), 100.6 (C-4), 77.7 (C-6'), 64.8 (C-6), 56.3 (3-OMe), 55.9 (2-OMe), 28.1 (2'-Me_2).

Lupeol **(4)**: Colourless crystalline flakes. ^{1}H and ^{13}C NMR data were in full agreement with lupeol [8]. HR-EIMS: *m/z*: 426.3862 (M^{+}).

12α-Acetoxy-12-deoxo-elliptone (8,9-Dimethoxy-6,6a,12,12a-tetrahydro-chromeno[3,4-b]furo[2,3-h]chromen-6-yl acetate) [9] **(5)**: Colourless needles from MeOH, m.p. 150-152 °C, ^{1}H NMR ($CDCl_3$) δ: 7.56 (1H, *d*, *J* = 2.4 Hz, H-2'), 7.19 (1H, *d*, *J* = 8.5 Hz, H-11), 7.10 (1H, *d*, *J* = 8.5 Hz, H-10), 6.86 (1H, *d*, *J* = 2.4 Hz, H-1'), 6.68 (1H, *s*, H-1), 6.43 (1H, *d*, *J* = 5.3 Hz, H-12), 6.42 (1H, *s*, H-4), 4.99 (1H, *m*, H-6a), 4.52 (1H, *t*,



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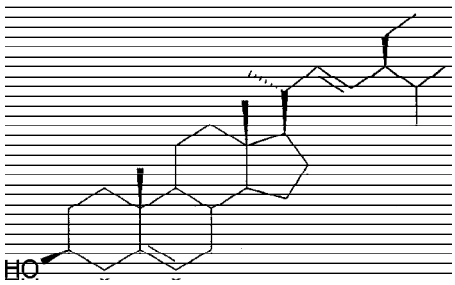

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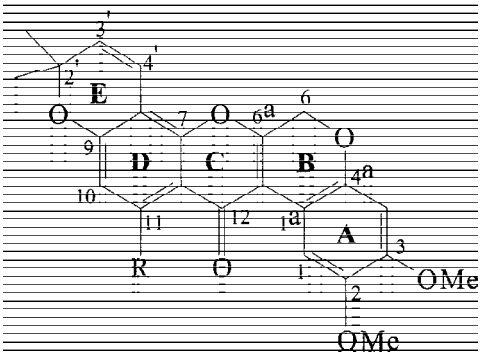
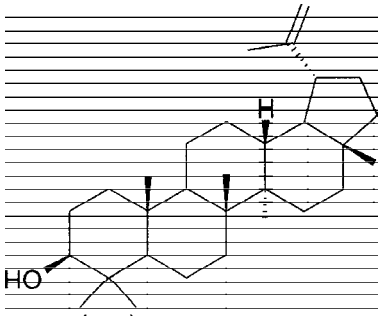


3a: R= OH
3b R= H



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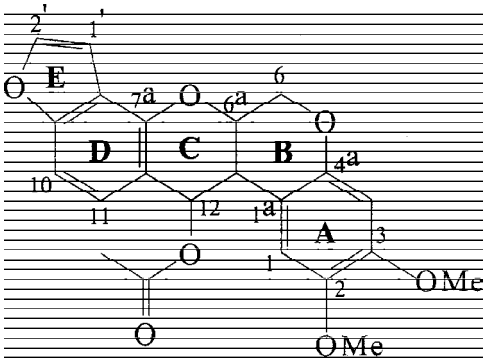

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J = 11.2 Hz, H-6α), 4.31 (1H, *dd*, *J* = 11.2, 5.3 Hz, H-6β), 3.84 (6H, **s**, 2/3-OMe), 3.63 (1H, *t*, *J* = 5.3 Hz, H-12a), 1.74 (3H, *s*, OAc). ^{13}C NMR ($CDCl_3$) δ: 170.0 ($COCH_3$), 156.8 (C-7a), 149.7 (C-3), 148.8 (C-4a), 144.3 (C-2'), 143.7 (C-2), 126.7 (C-11), 117.0 (C-11a), 112.4 (C-8), 111.4 (C-1), 108.7 (C-1a), 105.2 (C-10), 103.9 (C-1'), 100.4 (C-4), 69.2 (C-12), 66.6 (C-6a), 64.4 (C-6), 56.6 (OMe), 55.9 (OMe), 36.7 (C-12a), 20.8 ($COCH_3$).

3. Acknowledgments

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