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PTEROCARPOL AND TRITERPENES FROM *DAEMONOROPS DRACO**

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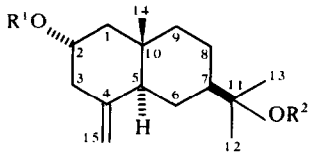
Key Word Index—*Daemonorops draco*; Palmae; eudesmane sesquiterpene; absolute configuration; 22-hydroxyhopanone; dipterocarpol; dammarenolic acid; oleanonic acid; oleanonic aldehyde; ursonic aldehyde.

Dragon's blood is a commercially available resin, obtained from trees of *Daemonorops draco* (Palmae) in south-east Asia. Previous research on the resin was concerned with red pigments [1], flavans [2], biflavonoids [3], deoxyproanthocyanidins [3], chalcones [2], secobiflavonoids [4] and diterpene acids [5].

We report here on the isolation and identification of several terpenoids. Some of them, i.e. the triterpenes 22-hydroxyhopanone, dipterocarpol, dammarenolic acid, oleanonic acid and oleanonic aldehyde, are already known as natural products. We also isolated a product that we assign the structure of ursonic aldehyde: this substance has not been previously isolated from natural sources or prepared by synthesis. However, the most interesting product was the very rare sesquiterpene pterocarpol, occurring only in *Pterocarpus santalinus* and *P. macrocarpus* (Leguminosae).

The structure of pterocarpol (**1a**) had been suggested by Seshadri *et al.* [6] and the physical and spectral data of our product agreed with those reported. The above structure was confirmed by spin decoupling experiments, by the ^{13}C NMR spectra of **1a** and its monoacetate **1b** (Table 1) and by induced shifts in the ^{1}H NMR spectrum of **1a** by Eu(dpm)$_3$ (Table 2).



1a $R^1 = H$, $R^2 = H$
1b $R^1 = Ac$, $R^2 = H$
1c $R^1 = Ac$, $R^2 = Ac$

As the absolute configuration of pterocarpol had been never ascertained, we submitted the product to Horeau's method [7]: the production of (+)-2-phenylbutyric acid indicated the *R* absolute configuration for C-2. Hence pterocarpol has the *normal* A/B-*trans* junction with equatorial 2α-OH, as depicted in **1a**.

The identification of the six triterpenes was performed by conventional methods (physical and spectral data, direct comparison with authentic specimens, chemical correlations).

We also had the opportunity of examining an original sample of the resin as it was collected on the tree. We found the same products (aromatic and terpenoids) as isolated from the commercial resin. Therefore we can rule out any hypothesis of adulteration with other resins like dammar or colophonia.

Table 1. ^{13}C NMR spectral data for compounds **1a** and **1b**

	1a	**1b**
C-1	51.03 *t*	46.80 *t*
C-2	67.89 *d*	70.72 *d*
C-3	46.55 *t*	42.31 *t*
C-4	148.21 *s*	147.08 *s*
C-5	49.41 *d*	49.36 *d*
C-6	40.88 *t*	40.75 *t*
C-7	49.23 *d*	49.29 *d*
C-8	24.69 *t*	24.64 *t*
C-9	22.00 *t*	21.81 *t*
C-10	35.25 *s*	35.52 *s*
C-11	72.82 *s*	72.85 *s*
C-12	27.36 *q*	27.35 *q*
C-13	27.12 *q*	27.17 *q*
C-14	17.25 *q*	16.69 *q*
C-15	107.97 *t*	109.12 *t*
Me-acet	—	21.32 *q*
CO-acet	—	170.68 *s*

EXPERIMENTAL

General methods. Mps are uncorr. CC was performed with Merck Si gel (0.05–0.20 mm), TLC with Merck HF_{254} Si gel plates, PLC on Merck 60 Si gel plates; spots were detected by spraying with H_2SO_4–MeOH or with cerium(IV) sulphate in H_2SO_4 (grey colour on heating). The purity of the products (sufficient for structural elucidation purposes) was checked by TLC, NMR and MS.

Isolation of constituents. A soln of commercial dragon's blood resin (100 g, provided by Ghezzi Society, Milan) in Me_2CO was filtered, mixed with 50 g Si gel, evapd and placed on top of a Si gel

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Table 2. ^{1}H NMR spectral shifts induced by adding Eu(dpm)$_3$ to 50 mg of **1a** in $CDCl_3$

	Amount of Eu(dpm)$_3$ added			
	—	10 mg	30 mg	60 mg
Angular Me	0.72	0.80	1.25	1.93
C(OH)(Me)$_2$	1.23	1.30	1.95	3.05
C=CH$_2$	4.85	4.90	5.17	5.55
	4.59	4.64	4.94	5.36
2β-H ax	3.90	4.22	6.25	9.45
3β-H eq	2.68	2.88	4.14	5.90
3α-H ax	—	—	3.78	5.90
1β-H eq	—	—	3.44	5.40
1α-H ax	—	—	2.98	5.14

column. After elution with hexane (1 l.), increasing amounts of EtOAc were added to the eluent. With hexane–EtOAc (4:1), a mixture of oleanonic and ursonic aldehydes was eluted; it was resolved by repeated prep. TLC with the same solvent. With hexane–EtOAc (2:1), a mixture of dipterocarpol, 22-hydroxyhopanone, oleanonic acid and monomeric flavans [2] was collected. Repeated prep. TLC in the same solvent gave the pure triterpenoids (R_f 0.42, 0.36 and 0.32, respectively). Elution with hexane–EtOAc (1:1) gave a very complex mixture in which the main constituents were bi- and tri-flavanoids [3]; dammarenolic acid and pterocarpol (R_f 0.13 and 0.08 in hexane–EtOAc, 2:1) were isolated by repeated prep. TLC with C_6H_6–Et_2O (2:1).

Pterocarpol (**1a**). Mp 100–102° (from C_6H_6), $[\alpha]_D^{20}$ + 34° ($CHCl_3$, *c* 0.29); also IR, MS and ^{1}H NMR data agree with those reported [6]. Acetylation with Ac_2O–pyridine at room temp. [6] gave the monoacetate **1b**, mp 87–88°. Our ^{1}H NMR spectrum ($CDCl_3$, 100 MHz) agreed with the data of Seshadri *et al.* [6], but an 8-line signal was evident at δ 2.70, due to the equatorial allylic 3β-H ($J_{3\beta.3\alpha} = 12$, $J_{3\beta.2\beta} = 5$, $J_{3\beta.1\beta} = 2$ Hz). On irradiation of 2β-H at 5.00, the signal collapsed into a double doublet ($J = 12$ and 2 Hz), whereas on irradiation at 1.70 it collapsed into a double doublet ($J = 5$ and 2 Hz). By contrast, irradiation of 3β-H at 2.70 transformed the 2β-H signal at 5.00 into a double doublet ($J = 11$ and 5 Hz). Acetylation with Ac_2O–pyridine at reflux [6] gave the oily diacetate **1c**; ^{1}H NMR ($CDCl_3$, 100 MHz): δ 0.76 (3H, *s*, *ang*-Me), 1.42 (6H, *s*, 2 × Me), 1.95 and 2.00 (3H each, *s*, 2 × MeCOO), other signals as in **1b**.

Horeau's method in pterocarpol (**1a**). (±)-2-Phenylbutyric anhydride (68 mg) was added to pterocarpol (**1a**) (48 mg) dissolved in 0.5 ml dry pyridine. By working up the reaction mixture according to ref. [7], (+)-2-phenylbutyric was isolated, $[\alpha]_D^{20}$ + 2.6° (pyridine, *c* 2.5).

Oleanonic aldehyde. Previously found in *Pistacia terebinthus* [8]. Mp 137° (from MeOH); MS *m/e*: 438 (M^+, $C_{30}H_{46}O_2$ requires 438.67), 409, 232, 203, 189, 133. ^{1}H NMR ($CDCl_3$, 60 MHz): δ 5.30 (1H, *m*, H-12), 9.65 (1H, *s*, CHO). IR ν_{max}^{nujol} cm^{-1}: 2700, 1735, 1715.

Ursonic aldehyde. Mp 130° (from MeOH); MS *m/e*: 438 (M^+, $C_{30}H_{46}O_2$ requires 438.67), 409, 232, 203, 189, 133, 70: for the significance of the ion *m/e* 70, see ref. [9]. ^{1}H NMR ($CDCl_3$, 60 MHz): δ 5.30 (1H, *m*, H-12), 9.60 (1H, *s*, CHO). IR ν_{max}^{nujol} cm^{-1}: 2700, 1735, 1715.

Dipterocarpol. Occurs in several Dipterocarpaceae. Mp 135° (from EtOAc); $[\alpha]_D^{20}$ + 65° ($CHCl_3$, *c* 0.81); IR ν_{max}^{nujol} cm^{-1}: 3450 and 1690; MS *m/e*: 424 (M − 18; $C_{30}H_{50}O_2$ requires 442.70), 355, 313. ^{1}H NMR ($CDCl_3$, 100 MHz): δ 0.91, 0.97, 1.03, 1.06, 1.10, 1.15, 1.65, 1.72 (3H each, *s*, 8 × Me), 5.18 (1H, *m*, H-24). The data agree with those of previous reports [10, 11]. Comparison (mmp, IR, NMR, MS) with an authentic specimen of dipterocarpol proved the identity of the two products. (Sample kindly provided by Dr. J. F. Biellmann, Strasbourg.)

22-Hydroxyhopanone [12]. Occurs in Dipterocarpaceae. Mp 255° (from EtOAc); $[\alpha]_D^{20}$ + 68° ($CHCl_3$, *c* 0.45). IR ν_{max}^{nujol} cm^{-1}: 3450 and 1710. MS *m/e*: 442 (M^+, $C_{30}H_{50}O_2$ requires 442.70), 424, 409, 384, 381, 205, 189, 95, 59: for this last peak, see ref. [13]. ^{1}H NMR ($CDCl_3$, 100 MHz): δ 0.80, 0.95, 0.99, 1.03, 1.04, 1.10, 1.20, 1.23 (3H each, *s*, 8 × Me). Comparison (mmp, IR, MS, GLC) with an authentic specimen of 22-hydroxyhopanone proved the identity of the two products. (Sample provided by Dr. J. F. Biellmann.)

Oleanonic acid. Found in Dipterocarpaceae and Hamamelidaceae. The raw product was methylated with CH_2N_2 and identified as the methyl ester. Mp 182° (from hexane–MeOH), $[\alpha]_D^{20}$ + 84° ($CHCl_3$, *c* 0.23). IR ν_{max}^{KBr} cm^{-1}: 1725 (sh) and 1705. MS *m/e*: 468 (M^+, $C_{31}H_{48}O_3$ requires 468.69), 409, 262, 249. ^{1}H NMR ($CDCl_3$, 100 MHz): δ 0.84, 0.90, 0.96, 1.04, 1.06 (3H each, *s*, 5 × Me), 1.10 (6H, *s*, 2 × Me), 5.30 (1H, *m*, H-12). The data agree with previous reports [14–16]. $NaBH_4$ reduction gave methyl oleanolate, mp 196°, identified by GLC (co-injection with an authentic sample). $LiAlH_4$ reduction gave erythrodiol, mp 236–238°, identified by comparison (mmp, IR) with an authentic specimen prepared by $LiAlH_4$ reduction of methyl oleanolate.

Dammarenolic acid. Occurs in Dipterocarpaceae. Mp 140° (from hexane–EtOAc), $[\alpha]_D^{20}$ + 42.5° ($CHCl_3$, *c* 0.2). IR ν_{max}^{nujol} cm^{-1}: 3400 (br.), 1710, 1640, 890. MS *m/e*: 440 (M − 18; $C_{30}H_{50}O_3$ requires 458.70), 371, 205. ^{1}H NMR ($CDCl_3$, 100 MHz): δ 0.86, 0.90, 1.00, 1.16, 1.64, 1.70, 1.74 (3H each, *s*, 7 × Me), 4.70 and 4.88 (*br. s*, 1H each, C=CH_2), 5.13 (1H, *m*, H-24). Methyl dammarenolate was prepared by CH_2N_2 treatment: mp 88° (from aq. MeOH), $[\alpha]_D^{20}$ + 43° ($CHCl_3$, *c* 0.67). These data agree with those reported [17–20] for dammarenolic acid and its methyl ester.

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