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Phytochemical Studies on Medicinal Plants, *Dracaenaceae* resin, of Socotra Island, Yemen

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Abstract
Phytochemical study on the *resin of Dracaenaceae* obtained from Socotra Island has been conducted. The separations of the chemical components were carried out by different chromatography techniques and their structures were elucidated by spectroscopic methods such as mass spectrometry (MS), ^{1}H and ^{13}C NMR and by comparison with those of previously reported data. Four compounds were isolated and identified as follows, one triterpenes was isolated which was identified as Stigmasterol and two were flavonoides which were identified as Pentahydroxy flavanone and Dracophaney, and fourth one identified as Orobol.
Keywords: Dracaena, Resins, Pentahydroxy-flavanone, Orobol, Stigmasterol, Dracophane, NMR.

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INTRODUCTION

Dracaena cinnabari (*Agavaceae*) is a perennial tree that is native to Socotra Island located on the Southern coast of Yemen (Bellakhdar, 1997; Gupta *et al.,* 2008). The tree produces a deep red resin that has been colorfully called the Dragon's blood or the two brother's Blood. The dry powdered resin is often used in the Arabian Peninsula, as well as in other countries (Prashanth *et al.,* 2006) as an herbal remedy for many ailments including analgesic, astringent, antiseptic, haemostatic, antiulcer and as abortifacient if taken during the first trimester of pregnancy (Al-Doais, 2001). Phytochemical studies have earlier led to the isolation of a number of flavonoids, the bioflavonoid cinnabarrine, triflavonoids, sterols and triterpenoids (Bahaffi *et al.,* 2004). Deraconaceae, a high-class product of the ancient world (Milburn, 1984). This red liquid extract from injured bark is known in Arabia as 'cinnabar'. The people from Socotra (Yemen) still use it to cure dysentery and gastric sores (Badib, 1991). It has been used as coloring agent and folk magic (Tao *et al.,* 2011). Dragon's blood of Soqotri *Dracaena cinnabari*, has been used as antimicrobial (Mothana and Lindequist, 2005; Kumar *et al.,* 2006), antiviral (Mothana *et al.,* 2006), antioxidant (Machala *et al.,* 2001), antitumor and cytotoxic activity (Al-Fatimi *et al.,* 2005).

The aim of this study was isolation and characterization of chemical compounds from *Dracaena cinnabari*.

MATERIALS AND METHODS

Collection of Plant Material

Dragon's blood from *Dracaena cinnabari* was collected in Socotra Island of Yemen in autumn 2014. Avoucher specimen of resin (JY22) is deposited at the Department of Natural Drugs, Faculty of Pharmacy, University Yemen Jordan (UYJB).

Extraction and Fractionation

Resins *of deraconaceae* in powder form (250 g) were extracted with ethanol (1.0 L) using Soxhlet apparatus (8 hours each). The combined extract was concentrated by using rotary evaporator to produce a crude ethyl ethanol extract (DR, 7 g). This extract was partitioned between hexane-ethanol (1:1, 300:300 ml) the ethanol layer was evaporated to obtain crude methanol extract (DR, 4 g). The DR fraction (2 g) was separated by using radial chromatography above silica gel with hexane-ethyl acetate in step grade polarity from 90:10 to 10:90. Fractions 1-20 were concentrated by rotary evaporator and subjected to silica gel TLC by using ethyl acetate and hexane (1:9).

Fractions 3 and 4 were combined to give D1 (4.0 mg) identified as *pentahydroxy-flavanone*. Fractions 5 and 6 were combined and separated further on radial chromatography (1 mm thickness) by using hexane-ethyl acetate with step gradient polarity to give D2 (2.6 mg) identified as *Stigmasterol*. The remaining powder of Resin *deraconaceae* (2 gm) was separated by using Colum

chromatography over silica gel with ethyl acetate – acetone \ in step gradient polarity from 90:10 to 10:90. Fractions 1-9 were concentrated by rotary evaporator and subjected to silica gel TLC by using chloroform and ethyl acetate (6:4). The combined fraction 1 and 3 (40 mg), separated further on PTLC by using hexane-ethyl acetate with step gradient polarity to give D3 (4.0 g) identified as Dracophane. Fractions 4, 5, and 7 (120 mg) were combined and subjected to radial chromatography (2 mm thickness) by using hexane-ethyl acetate with step gradient polarity to produce three pure compounds of D4 (3.6 mg) identified as 5, *7, 3', 4'-tetrahydroxy-isoflavone (orobol)*. These were accepted by relationship with data from earlier NMR and mass spectra.

Pentahydroxy-flavanone

Amorphous powder, $C_{15}H_{12}0_7$; (Table 1 and 2), (Figure 1).

Table 1. ^{1}H NMR chemical shifts of Pentahydroxy-flavanone in CD_3OD at 400 MHz

Atom	δ (ppm)	Atom	δ (ppm)
d, 8.4, 6'-H	7.29	*d,* 2.4, 6-H	5.77
d, 2.4, 5'-H	6.32	*d, 2.4*, 8-H	5.81
dd, 2.4, *3'*-H	6.28	*d,* 12.0, 2-H	4.79
d, 12.1, 3-H	4.99		

Table 2. ^{13}C NMR chemical shifts of Pentahydroxy-flavanone in CD_3OD at 100 MHz

Atom	δ (ppm)	Atom	δ (ppm)	Atom	δ (ppm)
C-4	196.54	C-4'	159.80	C-5'	107.60
C-7	168.21	C-2'	156.31	C-3'	104.12
C-5	165.90	C-6'	130.72	C-4a	102.11
C-8a	164.40	C-1'	117.12	C-8	97.22
C-6	96.00	C-2	75.30	C-3	74.86

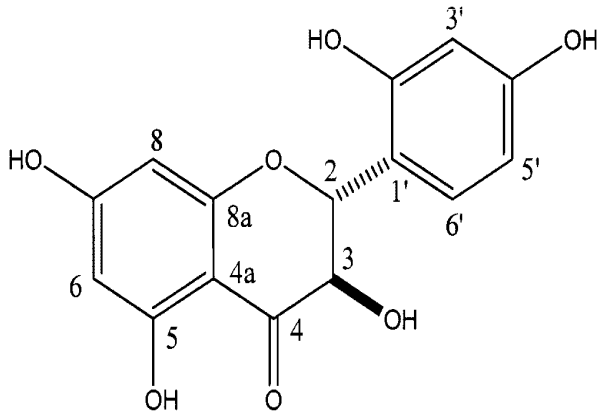

Fig. 1. Structure of Pentahydroxy-flavanone

Stigmasterol

White needles (3.5 mg). (Table 3 and 4), (Figure 2).

Table 3. ^{1}H NMR chemical shifts of Stigmasterol in $CDCl_3$ at 400 MHz

Atom	δ	Atom	δ
each 3H, Me × 6	0.67, 0.80, 0.82, 0.86, 0.92,1.02	s, H- 22	5.15
		s, H-23	5.01
t, H-6	5.36	m, H-3	3.53

Table 4. ^{13}C NMR chemical shifts of Stigmasterol in $CDCl_3$ at 100 MHz

Atom	δ (ppm)	Atom	δ (ppm)	Atom	δ (ppm)
C-5	141.1	C-13	40.4	C-28	25.0
C-22	138.0	C-20	39.5	C-15	23.6
C-23	130.2	C-12	38.9	C-21	20.1
C-6	122.0	C-4	36.6	C-11	19.2
C-3	71.6	C-1	35.4	C-27	18.8
C-14	56.2	C-10	35.1	C-26	18.3
C-17	51.7	C-8	31.6	C-19	17.9
C-24	49.9	C-7	30.9	C-29	11.8
C-9	48.3	C-16	28.1	C-18	11.0
C-25	45.8	C-2	27.3		

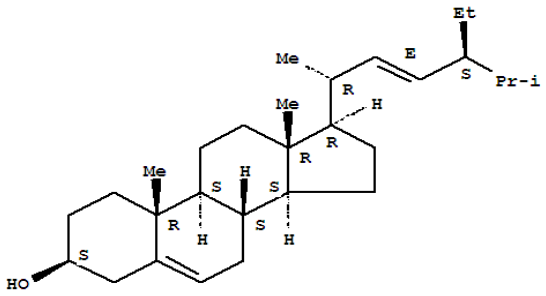

Fig. 2. Structure of Stigmasterol

Dracophane

Pinkish amorphous powder. Mp 293 °C. ($C_{48}H_{48}O_9$, 768.3298). (Table 5 and 6), (Figure 3).

Table 5. ^{1}H NMR chemical shifts of dracophane in DMSO-d_6 at 400 MHz

Atom	δ	Atom	δ	Atom	δ
OH-4'	8.98	H-3'	6.60	H-8β	2.53
OH-4"	8.98	H-3"	6.60	H-17β	2.53
OH-4"'	8.98	H-3"'	6.60	H-26α	2.40
OH-12	8.98	H-10	4.15	H-26β	2.40
OH-21	8.98	H-1	4.08	H-8α	2.28
OH-3	8.93	H-19	4.08	H-18β	2.28
H-7	7.21	OMe-5	3.36	H-27β	2.25
H-25	7.21	OMe-14	3.36	H-9β	2.25
H-16	7.10	OMe-23	3.36	H-17α	2.21
H- 2'	7.04	H-4	6.32	H-18α	2.21
H- 2"	7.04	H-13	6.32	H-9α	2.11
H- 2"'	7.04	H-22	6.32	H-27α	2.02

Table 6. ^{13}C NMR chemical shifts of dracophane in DMSO-d_6 at 100 MHz

Atom	δ (ppm)	Atom	δ (ppm)	Atom	δ (ppm)
C-14	156.41	C-2'	128.22	C-13	98.91
C-5	154.93	C-25	127.01	C-4	98.81
C-23	154.21	C-16	126.88	23-OCH_3	56.21
C-4"	154.81	C-7	126.43	14-OCH_3	54.04
C-4"'	154.81	C-20	122.54	5-OCH_3	53.35
C-4'	154.80	C-11	122.43	C-19	40.61
C-3	152.67	C-2	121.54	C-1	39.80
C-12	151.29	C-15	120.15	C-10	38.20
C-21	150.76	C-24	120.15	C-27	37.30
C-1'	135.73	C-6	119.85	C-9	36.53
C-1"	134.84	C-3"	114.52	C-18	35.56
C-1"'	134.84	C-3"'	114.52	C-17	29.76
C-2"	128.28	C-3'	114.49	C-8	28.51
C-2"'	128.28	C-22	99.02	C-26	26.02

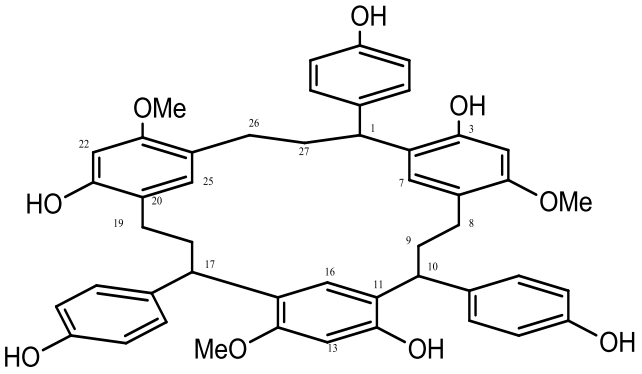

Fig. 3. Structure of Dracophane

Tetrahydroxy-isoflavone (orobol)

Light yellow compound (Table 7 and 8), (Figure 4).

Table 7. ^{1}H NMR chemical shifts of **Tetrahydroxy-isoflavone** in DMSO-d_6 at 400 MHz

Atom	δ (ppm)	Atom	δ (ppm)
OH	12.94	*d,* 8.1, 5'-H	6.76
s, 2-H	8.21	*d, 2.0*, 8-H	6.32
d, 1.6, 2'-H	6.97	*d,* 2.0, 6-H	6.12
d, 1.6, 8.0, 6'-H	6.80		

Table 8. ^{13}C NMR chemical shifts of **Tetrahydroxy-isoflavone** in DMSO-d_6 at 100 MHz

Atom	δ (ppm)	Atom	δ (ppm)	Atom	δ (ppm)
C-4	182.243	C-2	154.72	C-2'	116.90
C-7	163.30	C-4'	142.93	C-5'	113.48
C-5	161.16	C-3'	140.93	C-4a	100.55
C-8a	158.31	C-3	125.12	C-6	97.53
C-1'	124.07	C-6'	119.07	C-8	90.81

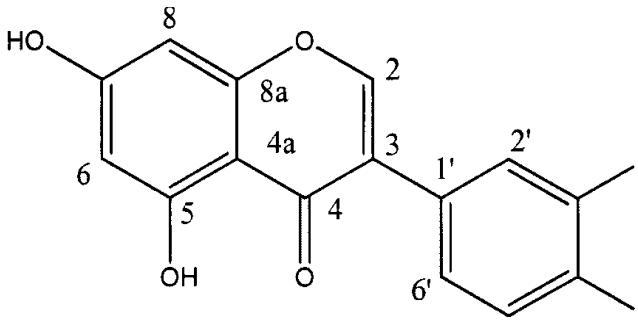

Fig. 4. Structure of Tetrahydroxy-isoflavone (orobol)

RESULTS AND DISCUSSION

Purification of the take out of the deraconaceae resin yielded compounds namely; (1), Pentahydroxy-flavanone, (2), Stigmasterol (3), Dracophane (4), Orobol; which have been studied in this paper.

The first compound was isolated as white needles. The ^{1}H and ^{13}C NMR spectra were characteristic of an isoflavone. ^{1}H NMR spectrum displayed a singlet for 2-H of the isoflavone at 68.207 (1H, s), signals of aromatic proton at δ 6.197 (H-6) and 6.345 (H-8), and signals of three aromatic proton at δ 6.984 (H -2'), 6.792 (H-6'), and 6.776 (H-5'). The chemical shift of carbonyl groups (C-4) was present at δ180.28. The aromatic protons were therefore placed in A-ring, while three aromatic proton signals of ABX system in B-ring. By detailed NMR comparison with those of reported isoflavones, compound 1 was identified as Pentahydroxy-flavanone (Agrawal 1989).

The second compound obtained was white powder. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum showed six methyl groups appeared at δ 0.67, 0.80, 0.82, 0.86, 0.92 and 1.02. The proton on the position 3 appeared as a multiplet at δ 3.53. Although olefinic protons were shown at δ 5.36, 5.15 and 5.01 (H-6, 17 &18). ^{13}C NMR (100 MHz, $CDCl_3$) showed signal of twenty nine carbons counting as six methyls, nine methylenes, eleven methane and three quaternary carbons. The measurements at δ140.0, 138.5, 129.5 and 122.6, appeared for alkene carbons. This compound was identified as Stigmasterol. Stigmasterol was reported in many plants *(*Singh *et al.,* 1978; Jamal *et al.,* 2008).

The third compound isolated was pinkish amorphous powder having melting point 293 °C and was identified as Dracophane. ^{1}H and ^{13}C NMR spectra showed three structural fragments exhibiting. Each fragment contained aromatic rings with 1,2,4,5-tetrasubstituted and side chains and has been designated as a substituted deoxotetrahydrochalcone. It showed proton signals characteristic of four 6-hydroxyphenyl cluster at δ8.98 (4', 4", 4"', 12, 21- OH), 8.93 (3-OH). Aliphatic protons appeared at δ 7.21 (*7, 25-H),* 7.10 (16-H), 4.15 (10-H), 4.08 (1, 19-H), 3.36 (5, 14, 23-OMe), 6.32 (4, 13, 22-H), 2.53 (8β, 17β-H),

2.40 (26α, 26β-H), 2.28 (8α, 18β-H), 2.25 (27β, 9β-H) 2.20 (17α,18α-H), 2.12 (9α-H), 2.03 (27α-H) (Vesela *et al.,* 2002). The fourth compound was also studied by ^{1}H and ^{13}C NMR spectra. ^{1}H NMR spectrum displayed a singlet for 2-H of the isoflavone at δ 8.207 (1H, s), a signals of aromatic proton appeared at δ 6.197 (6-H) and 6.345 (8-H) and proton signals of the three aromatic of an ABX system at δ 6.984 (2'-H), 6.792 (6'-H), and 6.776 (5'-H). ^{13}C NMR (100 MHz, DMSO-d_6) spectra exhibited fifteen carbons with two methyl, nine quaternary carbons and six methynes. Carbonyl groups appeared at 180.28, in the position C-4. The coupled aromatic protons were therefore placed in A-ring, while three aromatic proton signals of ABX system in B-ring. By detailed NMR comparison with those of reported isoflavones, compound 4 was identified 5, 7, 3', 4'-tetrahydroxy-isoflavone (Agrawal, 1989). A previous study has reported the isolation of six triterpenoids derivatives of lupane-type structure from the low-polar fraction of ethyl acetate extract of dry resin of dragon's blood tree (*Dracaena cinnabari* Balf.,), endemic to Socotra island, Yemen (Masaoud *et al.,* 2015).

CONCLUSION AND FINDINGS

The isolation and identification of Pentahydroxy-flavanone, Stigmasterol, Dracophane, Orobol, from Dracaena Resins was done and reported from this plant. The work was carried out by means of various physical (solvent extraction, radial chromatography) and spectral techniques.

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CONFLICT OF INTEREST

There is no conflict of interest.

REFERENCES

Agrawal, P., 1989. Carbon - ^{13} NMR of Flavonoids. Elsevier Science, 199-200.

Al-Doais, M.A. 2001. The world initiation for announcing Socotra archipelago as man-biosphere natural reserve. Al-Bayan, III: 242-268.

Al-Fatimi, M., Friedrich, U., Jenett-Siems, K., 2005. Cytotoxicity of plants used in traditional medicine in Yemen. Fitoterapia., 76: 355-358.

Bahaffi, S.O.S., Bahaffi, A.A., Adel-Mogib, M., 2004. Flavans and chalcones from dragon's blood of Dracaena cinnabari. J. Saudi Chem. Soc., 8(2): 313-315.

Badib, A.S., 1991. The medicinal plants of Yemen. Maktabah Alirsad, Sanaa.

Bellakhdar, J., 1997. La Pharmaacope´e Marocaine Traditionnelle. Me´decine Arabe Ancienne et Savoirs Populaires, Ibis Press, Paris.

Gupta, D., Bleakley, B., Gupta, R.K., 2008. Dragon's blood: Botany, chemistry and therapeutic uses (Review Article). J. Ethnopharmacol., 115(3): 361-380.

Jamal, A.K., Yaacob, W.A., Din, L.B., 2008. A Chemical Study on *Phyllanthus reticulatus*. J. Phys. Sci., 19(2): 45-50.

Kumar, V.P., Chauhan, N.S., Padh, H., Rajani, M., 2006. Search for antibacterial and antifungal agents from selected Indian medicinal plants. J. Ethnopharmacol., 107: 182-188.

Machala, M., Kubiinova, R., Horavova, P., Suchy, V., 2001. Chemoprotective potentials of homoisoflavonoids and chalcones of Dracaena cinnabari: modulations of drug metabolizing enzymes and antioxidant activity. Phytother. Res., 15: 114-118.

Masaoud, M., Hussein, K., Ahmed,A.H., Al.Maqtari, M.A., 2015. Lupane-type triterpenoids derivatives from resin of the Socotra Dragon tree (*Dracaena cinnabari* Balf., agavaceae). World J. Pharm. Pharm. Sci., 4(4): 182-194.

Milburn, M. 1984. Dragon's blood in East and West Africa, Arabia and the Canary Islands. Africa. 39: 486-493.

Mothana, R.A.A., Lindequist, U., 2005. Antimicrobial activity of some medicinal plants of the island Soqotra. J. Ethnopharmacol., 96: 177-181.

Mothana, R.A.A., Mentel, R., Reiss, C., Lindequist, U., 2006. Phytochemical screening and antiviral activity of some medicinal plants from the island Soqotra. Phytother. Res., 20: 298-302.

Prashanth K.V., Chauhan N.S., Padh H., Rajani M.B.V., 2006. Search for antibacterial and antifungal agents from selected Indian medicinal plants. J. Ethnopharmacol. 107(2): 182-188.

Singh, H., Kapoor, V.K., Piozzi, F., Passannanti, S. Paternostro, M., 1978. Isomotiol, a new triterpene from *Strychnos potatorum*. Phytochem., 17(1): 154-155.

Yi, T., Chen, H.B., Zhao, Z.Z., Yu, Z.L., Jiang, Z.H., 2011. Comparison of the chemical profiles and anti-platelet aggregation effects of two "Dragon's Blood" drugs used in traditional, Chinese medicine. J. Ethnopharmacol., 133(2): 796-802.

Vesela, D., Marekb, R., Ubikc, K., Lunerova, K. Sklenar, V., Suchy, V., 2002. Dracophane, a metacyclophane derivative from the resin of *Dracaena cinnabari* Balf. Phytochem., 61: 967-970.