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# DAMALACHAWIN, A TRIFLAVONOID OF A NEW STRUCTURAL TYPE FROM DRAGON'S BLOOD OF *DRACAENA CINNABARI*

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**Key Word Index**—*Dracaena cinnabari*; Agavaceae; resin; triflavonoid; damalachawin.

**Abstract**—A new triflavonoid, damalachawin, was isolated from dragon's blood of *Dracaena cinnabari*. Its structure was established mainly by NMR spectroscopy.

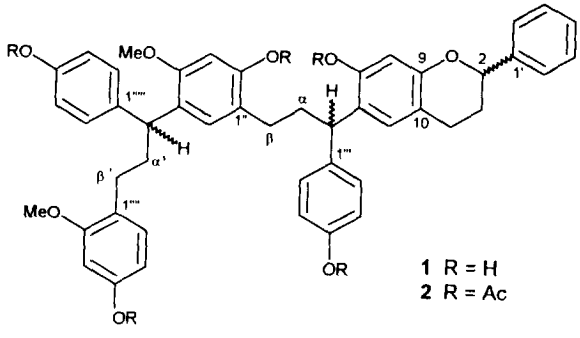
## INTRODUCTION

The dragon's blood tree, *Dracaena cinnabari*, growing endemic in the Island of Socotra (Yemen) is used in folk medicine [1]. Phytochemical studies of this plant have previously led to the isolation of a number of flavonoids [2, 3], the new biflavonoid cinnabarone [4], as well as a series of sterols and triterpenoids [5]. In continuation of our work on the constituents of dragon's blood from *D. cinnabari*, we isolated a triflavonoid of a new structural type, for which the name damalachawin is proposed according to the Arab designation for the resin with the meaning of brother's blood. Its structure was determined as **1** mainly on the basis of NMR spectroscopy as outlined below.

## RESULTS AND DISCUSSION

The elemental composition of **1** was shown by high-resolution mass spectroscopy to be $C_{47}H_{46}O_8$ (high resolution of the fragments $C_{32}H_{32}O_6$ and $C_{15}H_{14}O_2$, see Experimental). Ions at *m/z* 587, 407, 331, 151 and 137 can be explained by benzyl cleavage. Further ions at *m/z* 512, 482, 256 and 226 are formed by splitting off of monomeric flavonoid units.

One- and two-dimensional NMR methods, including the inverse technique, were used to provide signal assignments and to determine the structure of damalachawin (**1**) and its acetate (**2**). The methods applied were $^{13}C$-attached proton test, 2D H–H COSY 90, 2D H–H delayed COSY 45, 2D H–H ROESY, proton-detected heteronuclear chemical shift correlation via $^1J$(C, H) (HMQC) and heteronuclear multiple bond connectivity (HMBC) experiments. The proton–proton coupling networks and the proton–carbon assignments via $^1J$(C, H) could be analysed by H–H COSY and HMQC techniques (Tables 1 and 2).




The connectivities of the aromatic rings with the aliphatic side-chains were detected by the H–H delayed COSY 45 technique which allowed the determination of H–H coupling patterns via $^4J$(H, H) and by HMBC which indicated C–H coupling patterns via $^nJ$(C, H) ($n$ = 2–4). Long-range H–H couplings were found for **1** between CH ($\delta$4.18) and H-$\beta$ ($\delta$2.4), H-5 ($\delta$6.83) and H-2‴/H-6‴ ($\delta$7.08); between CH′ ($\delta$4.16) and H-$\beta'$ ($\delta$2.4), H-6″ ($\delta$6.86) and H-2⁗/H-6⁗ ($\delta$7.06); between H-2 ($\delta$4.98), H-4 ($\delta$2.60 and 2.83) and H-2′/H-6′ ($\delta$7.40); between H-$\beta$ ($\delta$2.4) and H-6″ ($\delta$6.86), as well as between H-$\beta'$ ($\delta$2.4) and H-6⁗ ($\delta$6.81).

In addition, the connectivities of the aromatic rings and aliphatic side-chains could be recognized by analysing the NOEs using ROESY experiments. Besides the expected NOEs, strong effects were found between the 4″-methoxy group and H-3″, as well as between 2⁗-OMe and H-3⁗, but not H-5⁗, as in the previously reported cinnabarone [3], which indicate 4″- and 2⁗-positions for the methoxy groups.

We used proton-detected multiple bond $^1H$–$^{13}C$ correlation (HMBC) to obtain the assignments of all quaternary carbons and to confirm the connectivities indepen-

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Table 1. $^1$H NMR chemical shifts (ppm) and H–H coupling constants ($J$/Hz) of compounds **1** and **2**

| | **1** ($CD_3OD$) | **2** ($CDCl_3$) |
|---|---|---|
| H-α | 2.04–2.15 (2H, *m*) | 2.17–2.21 (2H, *m*) |
| H-β | 2.38–2.44 (2H, *m*) | 2.49–2.53 (2H, *m*) |
| CH | 4.18 (1H, *t*, 7.5 Hz) | 3.96 (1H, *t*, 7.2 Hz) |
| H-α′ | 2.04–2.15 (2H, *m*) | 2.17–2.21 (2H, *m*) |
| H-β′ | 2.38–2.44 (2H, *m*) | 2.49–2.53 (2H, *m*) |
| CH′ | 4.16 (1H, *t*, 7.3 Hz) | 3.96 (1H, *t*, 7.2 Hz) |
| H-2 | 4.98 (1H, *m*) | 5.01 (1H, *dd*, 10.5; 1.9 Hz) |
| H-3 | 1.95/2.11 (2H, *m*) | 2.04/2.14 (2H, *m*) |
| H-4 | 2.60/2.83 (2H, *m*) | 2.73/2.92 (2H, *m*) |
| H-5 | 6.83 (1H, *s*) | 6.97 (1H, *s*) |
| H-8 | 6.26 (1H, *s*) | 6.56 (1H, *s*) |
| H-2′, H-6′ | 7.40 (2H, *d*, 7.3 Hz) | 7.38 (2H, *m*) |
| H-3′, H-5′ | 7.34 (2H, *t*, 7.3 Hz) | 7.38 (2H, *m*) |
| H-4′ | 7.27 1H, *t*, 7.3 Hz) | 7.31 (1H, *t*, 7.2 Hz) |
| H-3″ | 6.35 (1H, *s*) | 6.54 (1H, *s*) |
| H-6″ | 6.86 (1H, *s*) | 7.01 (1H, *s*) |
| H-2‴, H-6‴ | 7.08 (2H, *d*, 8.2 Hz) | 7.17 (2H, *d*, 8.2 Hz) |
| H-3‴, H-5‴ | 6.67 (2H, *d*, 8.2 Hz) | 6.98 (2H, *d*, 8.2 Hz) |
| H-3⁗ | 6.34 (1H, *d*, 2.4 Hz) | 6.48 (1H, *d*, 2.2 Hz) |
| H-5⁗ | 6.24 (1H, *dd*, 8.0; 2.4 Hz) | 6.58 (1H, *dd*, 8.1; 2.2 Hz) |
| H-6⁗ | 6.81 (1H, *d*, 8.0 Hz) | 6.94 (1H, *d*, 8.1 Hz) |
| H-2⁗′, H-6⁗′ | 7.06 (2H, *d*, 8.2 Hz) | 7.21 (2H, *d*, 8.2 Hz) |
| H-3⁗′, H-5⁗′ | 6.66 (2H, *d*, 8.2 Hz) | 6.98 (2H, *d*, 8.2 Hz) |
| 4″ -OMe | 3.68 (3H, *s*) | 3.70 (3H, *s*) |
| 2⁗ -OMe | 3.72 (3H, *s*) | 3.73 (3H, *s*) |
| H- Ac | - | 2.02; 2.16; 2.26; 2.27; 2.28 (15H, *s*) |

Table 2. $^{13}$C NMR chemical shifts (ppm) of compounds **1** and **2**

| | **1** ($CD_3OD$) | **2** ($CDCl_3$) | | **1** ($CD_3OD$) | **2** ($CDCl_3$) |
|---|---|---|---|---|---|
| C-α | 37.5[a] | 34.8[g] | C-5″ | 124.4 | 127.9[i] |
| C-β | 29.7[b] | 28.5 | C-6″ | 130.0 | 129.1 |
| C-H | 43.2[c] | 43.0[h] | C-1‴ | 138.3 | 142.2[k] |
| C-α′ | 37.4[a] | 35.1[g] | C-2‴, C-6‴ | 130.0 | 128.8[l] |
| C-β′ | 29.6[b] | 28.5 | C-3‴, C-5‴ | 115.7 | 121.4 |
| C-H′ | 43.1[c] | 43.2[h] | C-4‴ | 155.9 | 148.9 |
| C-2 | 79.0 | 77.9 | C-1⁗ | 123.3 | 127.6 |
| C-3 | 25.6 | 30.0 | C-2⁗ | 159.7 | 158.1 |
| C-4 | 31.7 | 25.2 | C-3⁗ | 99.7 | 104.4 |
| C-5 | 129.5 | 128.5 | C-4⁗ | 157.5[e] | 149.9 |
| C-6 | 126.5 | 130.0 | C-5⁗ | 107.5 | 112.9 |
| C-7 | 155.0 | 147.3 | C-6⁗ | 131.1 | 130.1 |
| C-8 | 103.9 | 111.0 | C-1⁗′ | 138.5 | 142.1[k] |
| C-9 | 154.6[d] | 153.8 | C-2⁗′, C-6⁗′ | 130.0 | 128.9[l] |
| C-10 | 113.7 | 119.8 | C-3⁗′, C-5⁗′ | 115.7 | 121.4 |
| C-1′ | 143.6 | 141.6 | C-4⁗′ | 156.0 | 147.3 |
| C-2′, C-6′ | 127.0 | 126.1 | 4″-OMe | 55.7[f] | 55.5[m] |
| C-3′, C-5′ | 129.3 | 128.5 | 2⁗′-OMe | 55.6[f] | 55.4[m] |
| C-4′ | 128.6 | 128.5 | Ac-Me | — | 20.8–21.3 |
| C-1″ | 122.8 | 127.5[j] | C=O | — | (5C) |
| C-2″ | 154.5[d] | 156.2 | | | 169.3–169.6 |
| C-3″ | 99.9 | 105.3 | | | (5C) |
| C-4″ | 157.3[e] | 141.8 | | | |

[a–m]May be reversed.

dently. All expected correlations via $^2J$(C, H) and $^3J$(C, H) according to structures **1** and **2** were found.

The $^1$H and $^{13}$C NMR spectra of the acetyl derivative **2** proved the existence of five acetoxy groups (corresponding to five hydroxy groups in **1**). The expected upfield shifts for the *ipso* carbons of the acetate were observed.

From these data structure **1** is established for this new triflavonoid which is composed of a flavan and two deoxotetrahydrochalcone moieties. It differs mainly from cinnabarone [3] by replacement of the keto group by a 7-hydroxyflavan-6-yl group and hydrogen.

## EXPERIMENTAL

NMR expts were carried out at 500 MHz ($^1$H) and 126 MHz ($^{13}$C). The delay $\tau_1$ in HMQC and HMBC was adjusted to $^1J$(C, H) = 150 Hz. The delay $\tau_2$ in HMBC was set to 70 ms according to long-range coupling around 7 Hz and to 140 ms according to long-range coupling around 3 Hz.

*Plant material.* Dragon's blood from *D. cinnabari* Balf. fil. was collected in Socotra Island of Yemen in the summer of 1992. A voucher specimen is deposited at the Institute of Plant Biochemistry, Halle.

*Damalachawin* (**1**). Powdered resin was successively extracted with *n*-hexane, $CHCl_3$ and MeOH. Evapn of MeOH *in vacuo* gave a residue, which was chromatographed on silica gel with $CHCl_3$–MeOH (19:1), on silica gel with toluene–EtOAc–HOAc (70:30:1), on LiChroprep RP-18 with MeCN–$H_2O$–HOAc (50:50:0.2) and on Sephadex LH-20 with MeOH; yield 0.04%. Amorphous. $R_f$ 0.55 [Merck TLC plates RP-18 $F_{254}S$, MeCN–$H_2O$–HOAc (40:10:1), detection by vanillin–$H_3PO_4$ at 120°]. UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 214 (4.60), 223sh (4.52), 285 (4.06). EIMS (70 eV) *m/z* (rel. int.): 738 $[M]^+$ (5), 587 (3), 512.2120 ($C_{32}H_{32}O_6$, calc. 512.2199) (5), 482.2071 ($C_{31}H_{30}O_5$, calc. 482.2093) (17), 407 (3), 331.1333 ($C_{22}H_{19}O_3$, calc. 331.1334) (100), 256.1080 ($C_{16}H_{16}O_3$, calc. 256.1099) (24), 226.1005 ($C_{15}H_{14}O_2$, calc. 226.0994) (19), 151.0733 ($C_9H_{11}O_2$, calc. 151.0759) (12), 137.0591 ($C_8H_9O_2$, calc. 137.0602) (37).

*Pentaacetate* (**2**). Amorphous. $[\alpha]_D^{22}$ + 8.5° ($CHCl_3$; *c* 0.45). EIMS (70 eV) *m/z* (rel. int.): 948 $[M]^+$ (8), 906 $[M - CH_2CO]^+$ (39), 864 $[M - 2CH_2CO]^+$ (8), 713 (7), 671 (5), 638 (14), 596 (2), 491 (10), 477 (15), 415 (14), 373 (72), 331 (32), 285 (18), 255 (18), 227 (18), 137 (100).

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