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# STEROLS AND TRITERPENOIDS FROM *DRACAENA CINNABARI*

MOHAMED MASAOUD, JÜRGEN SCHMIDT and GÜNTER ADAM*

Institute of Plant Biochemistry, Weinberg 3, D-06120 Halle/S., Germany

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**Key Word Index**—*Dracaena cinnabari*; Agavaceae; phytosterols; triterpenoids.

**Abstract**—Cholest-4-en-3-one, 4α-methylcholest-7-en-3β-ol, 4α,14α-dimethylcholest-8-en-3β-ol, 31-norcycloartanol, lanost-7-en-3β-ol, cholesterol, campesterol, stigmasterol, sitosterol, stigmastanol, stigmast-22-en-3β-ol, cycloartanol, 24-methylenecycloartanol, lupeol and betulin have been isolated from resin (dragon's blood) or roots of *Dracaena cinnabari* and identified by capillary GC and GC-mass spectrometry.

## INTRODUCTION

The medicinal plant *Dracaena cinnabari* Balf. fil., growing endemic in the Socotra Island of Yemen, is known as dragon's blood tree. Phytochemical study of this plant has previously led to the isolation of several flavonoids [1, 2] and with cinnabarone to a new type of biflavonoid [3]. We now report the isolation and identification of sterols and triterpenoid constituents of this plant.

## RESULTS AND DISCUSSION

The sterols 4α-methylcholest-7-en-3β-ol (lophenol) [4], 4α,14α-dimethylcholest-8-en-3β-ol (31-nordihydrolanosterol) [5], 31-norcycloartanol [4] and lanost-7-en-3β-ol [6] were isolated from resin of *D. cinnabari* and their structures have been identified on the basis of the mass spectra of the corresponding acetate by comparison with reported data. Furthermore, the elution order in GC compared with other sterols are in agreement with the supposed structures [7]. Cholest-4-en-3-one, which has been previously isolated from the sponges *Stelleta clarella* [8] and *Cinachyra terentina* [9], was identified on the basis of mass spectral fragmentation compared with literature data. Of special interest is the occurrence of the scarce mono- and dimethylsterols as well as of cholest-4-en-3-one in resin of *D. cinnabari* whereas lophenol is the dominating component (86%).

Cycloartanol and 24-methylenecycloartanol [10], isolated from resin, have been identified from GC and GC-mass spectra by comparison with authentic samples. The resin and roots of *D. cinnabari* show a different pattern of sterols and triterpenes (Tables 1 and 2). The lupane type triterpenes lupeol and betulin represents the major compounds in roots of *D. cinnabari*. Their structures were identified by comparison of the spectroscopic (MS, $^{13}$C NMR) and physical data (mp, $[\alpha]_D$) compared with the literature [11–13]. While betulin only occurs in roots, lupeol could be detected both in roots and resin of *D. cinnabari*. In resin lupeol was identified by GC-mass spectra (Table 1). The phytosterols cholesterol, campesterol, stigmasterol, sitosterol, stigmast-22-en-3β-ol and stigmastanol could be determined from GC and GC-mass spectra as their acetates by comparison with the reported data [7, 10, 14]. The configurations at C-24 were not determined and are assumed to be 24α in accord with the major sterols found in many higher plants.

## EXPERIMENTAL

*Plant material.* Dragon's blood and roots from *D. cinnabari* were collected in Socotra Island of Yemen in summer 1992. Voucher specimens of resin and roots are deposited at the Institute of Plant Biochemistry, Halle.

*Extraction and isolation.* The powdered resin (500 g) was extracted with *n*-hexane and the extract was concentrated *in vacuo* (40°). The residue (2.8 g) was chromatographed on a silica gel column (Merck 60, 0.063–0.20 mm) and eluted with *n*-hexane–EtOAc (9:1) in 20 ml frs. The combined frs 5–7 were evaporated and the residue (5 mg) was acetylated with $Ac_2O$–pyridine. The acetate mixture was examined by capillary GC and GC-MS to reveal cholest-4-en-3-one, lanost-7-en-3β-ol, cycloartanol, lupeol and 24-methylenecycloartanol (Table 1).

Frs 9–12 were combined and evaporated. The residue (7 mg) was also acetylated with $Ac_2O$–pyridine and the acetate mixture was determined by GC and GC-MS. 4α, 14α-Dimethylcholest-8-en-3β-ol, 4α-methylcholest-7-en-3β-ol and 31-norcycloartanol were identified (Table 1). The dried roots (500 mg) of *D. cinnabari* were successively extracted with *n*-hexane and $CH_2Cl_2$. The *n*-hexane extract was evaporated to dryness *in vacuo* and the residue (2.6 g) was chromatographed on silica gel (Merck 60, 0.063–0.20 mm), eluting with gradient of *n*-hexane–EtOAc mixture. Elution with *n*-hexane–EtOAc

*Author to whom correspondence should be addressed.

Table 1. Retention time of sterols and triterpenoids in the resin of *D. cinnabari*

| Compound* | $RR_t$** |
|---|---|
| Cholest-4-en-3-one | 1.89 |
| 4α,14α-Dimethylcholest-8-en-3β-ol | 2.26 |
| 4α-Methylcholest-7-en-3β-ol | 2.45 |
| 31-Norcycloartanol | 2.54 |
| Lanost-7-en-3β-ol | 2.85 |
| Cycloartanol | 2.93 |
| Lupeol | 3.14 |
| 24-Methylenecycloartanol | 3.58 |

*Determined as acetate.

**Relative retention time ($RR_t$) with respect to 5α-cholestane.

Table 2. Phytosterol composition in roots of *D. cinnabari*

| Phytosterol* | $RR_t$** | Composition |
|---|---|---|
| Cholesterol | 1.99 | 0.6 |
| Campesterol | 2.46 | 0.5 |
| Stigmasterol | 2.62 | 40.0 |
| Stigmast-22-en-3β-ol | 2.68 | 2.0 |
| Sitosterol | 2.95 | 54.0 |
| Stigmastanol | 3.01 | 2.9 |

*Determined as acetate.

**Relative retention time ($RR_t$) with respect to 5α-cholestane.

(19:1) gave lupeol (1.2 g). Elution with *n*-hexane–EtOAc (9:1) afforded the phytosterol fraction, which was acetylated with $Ac_2O$–pyridine and examined by GC and GC-MS (Table 2). From the $CH_2Cl_2$ extract (4.2 g) on silica gel chromatography, eluting with *n*-hexane–EtOAc (8:2) betulin (940 mg) was isolated.

*Capillary gas chromatography.* Carlo Erba MEGA 5160; column PB-1 (Werner Günther Analysentechnik, 50 m × 0.32 mm; 0.25 film thickness); inj. temp. 225°; column temp. 270° (isothermal); detection FID (temp. 290°); carrier gas $N_2$, flow rate 1.5 ml $min^{-1}$, split injection (split ratio 1:20).

*GC-MS.* MD 800 (Fisons Instruments); EI (70 ev); column DB-1 (15 m × 0.25 mm; 0.25 μm film thickness), inj. temp. 250°, temp. program: 170° for 1 min then elevated to 270° within 25 grd $min^{-1}$, then raised to 290° at a rate of 2 grd $min^{-1}$; carrier gas He, flow rate 0.8 ml $min^{-1}$.

*Cholest-4-en-3-one.* MS *m/z* (rel. int.): 384 $[M]^+$ (33), 369 (13), 342 (22), 327 (11), 299 (14), 272 (13), 261 (38), 260 (33), 229 (77), 187 (15), 161 (10), 149 (24), 147 (31), 135 (25), 124 (100), 107 (24), 91 (22).

*4α,14α-Dimethylcholest-8-en-3β-yl acetate.* MS *m/z* (rel. int.): 456 $[M]^+$ (13), 442 (33), 441 (86), 397 (3), 382 (17), 381 (92), 327 (17), 301 (5), 287 (18), 273 (23), 242 (20), 229 (28), 227 (33), 215 (39), 201 (44), 173 (44), 161 (55), 159 (67), 121 (68), 119 (81), 105 (95), 95 (100), 69 (76).

*4α-Methylcholest-7-en-3β-yl acetate.* MS *m/z* (rel. int.): 442 $[M]^+$ (77), 427 (16), 382 (10), 367 (20), 329 (8), 287 (11), 270 (21), 269 (100), 243 (31), 227 (68), 187 (13), 173 (23), 161 (41), 147 (33), 119 (33), 105 (66), 95 (78).

*31-Norcycloartanyl acetate.* MS *m/z* (rel. int.): 456 $[M]^+$ (2), 442 (5), 397 (8), 396 (32), 381 (43), 343 (6), 341 (11), 288 (11), 283 (25), 227 (11), 207 (17), 189 (24), 175 (41), 147 (44), 133 (44), 121 (50), 109 (55), 107 (72), 95 (100).

*Lanost-7-en-3β-yl acetate.* MS *m/z* (rel. int.): 470 $[M]^+$ (10), 456 (20), 455 (60), 412 (7), 397 (7), 396 (31), 395 (100), 370 (8), 341 (5), 327 (4), 289 (9), 273 (10), 229 (22), 207 (14), 175 (20), 161 (20), 147 (18), 124 (17).

*Cycloartanyl acetate.* MS *m/z* (rel. int.): 470 $[M]^+$ (10), 455 (43), 395 (74), 341 (3), 301 (4), 255 (7), 95 (100).

*24-Methylenecycloartanyl acetate.* MS *m/z* (rel. int.): 482 $[M]^+$ (9), 422 (32), 407 (43), 379 (40), 353 (17), 300 (28), 297 (20), 285 (15), 203 (41), 147 (61), 95 (100).

*Stigmast-22-en-3β-yl acetate.* MS *m/z* (rel. int.): 456 $[M]^+$ (57), 441 (6), 353 (49), 344 (49), 329 (17), 315 (60), 302 (16), 269 (15), 257 (100), 229 (8), 215 (23), 163 (33), 123 (50).

*Lupeolyl acetate.* MS *m/z* (rel. int.): 468 $[M]^+$ (23), 453 (13), 408 (79) 393 (11), 357 (10), 341 (6), 297 (8), 249 (15), 218 (100), 203 (45), 189 (82).

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