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# DITERPENOID RESIN ACIDS OF *DAEMONOROPS DRACO*

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**Key Word Index**—*Daemonorops draco*; Palmae; Dragon's Blood; diterpenoid acids.

**Abstract**—Chromatography of a cyclohexane extract of commercial "dragon's blood" resin yielded a fraction containing pimaric, isopimaric, dehydroabietic and abietic acids. A fifth component of the mixture was tentatively identified as sandaracopimaric acid.

## INTRODUCTION

"DRAGON'S BLOOD" resin (Drachenblut, Sang-Dragon) is commercially available from South East Asia, in the form of granules or of a reddish powder. It is obtained from the exudate of the fruits of *Daemonorops draco*.[1] The commercial resin has been previously investigated for the red pigments, dracorubin and dracorhodin[2] and recently some flavonoid compounds were isolated.[3,4] Chromatography of a cyclohexane extract of the resin also yields some terpenoid fractions; we report here on a fraction containing some diterpenic acids.

## RESULTS AND DISCUSSION

The occurrence of $C_{20}$ derivatives was reported by Hesse,[5] who reported that the resin contained up to 50% by weight of abietic acid and of a similar unidentified acid. We have isolated from the commercial resin a small quantity of a mixture of at least five acids identified by GLC and GC-MS analysis.

The mixture of the acids and of their methyl esters gave MS characteristic of known resin acids. GLC analysis of the Me esters on five different columns showed five prominent peaks (Table 1); the identification of two peaks (*D* and *E*) was made by co-injection with authentic specimens of methyl dehydroabietate and methyl abietate; the remaining three

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[1] As to the origin of this resin, also known as "Indian" dragon's blood, see FRÄNKEL, S. and DAVID, E. (1927) *Biochem. Z.* **187,** 146. Other red resins, no longer commercially available, were extracted in the past from the bark of quite different plants, and named "American", "Mexican", "Socotra" and "Canary" dragon's blood; the extractives of the latter one (from *Dracaena draco*) are totally unlike those of "Indian" dragon's blood.

[2] DEAN, F. M. (1963) Naturally Occurring Oxygen Ring Compounds, pp. 412, 491, Butterworth, London.

[3] CARDILLO, G., MERLINI, L., NASINI, G. and SALVADORI, P. (1971) *J. Chem. Soc.* (c) 3967.

[4] MERLINI, L. and NASINI, G. In preparation.

[5] HESSE, G. (1936) *Ann.* **524,** 14.

peaks were tentatively identified as methyl pimarate, methyl sandaracopimarate and methyl isopimarate, on the basis of their relative retention data.[6–8]

TABLE 1. GLC ANALYSIS OF THE METHYL ESTERS OF THE RESIN ACIDS FROM *Daemonorops draco*

| Compound | SE-30 | Apiezon L | Carbowax 20M | QF-1 | XE-60 |
|---|---|---|---|---|---|
| A | 1·0 | 1·0 | 1·0 | 1·0 | 1·0 |
| B | 1·06* | 1·07* | 1·09 | 1·03* | 1·08* |
| C | 1·17 | 1·26 | 1·37 | 1·09 | 1·31 |
| D | 1·26 | 1·37 | 2·03 | 1·14 | 1·55 |
| E | 1·47 | 1·71 | 2·03 | 1·21 | 1·83 |
| Methyl dehydroabietate | 1·26 | 1·37 | 2·03 | 1·14 | 1·55 |
| Methyl abietate | 1·47 | 1·71 | 2·03 | 1·21 | 1·83 |

Retention data relative to compound A—methyl pimarate.
* Partially resolved as a shoulder.

The same mixture was subjected to GLC–MS analysis; peaks *A*, *C*, *D*, *E* gave MS in full agreement with those reported[8] for methyl pimarate, methyl isopimarate, methyl dehydroabietate and methyl abietate respectively. No MS could be recorded for peak *B*, as it was weak and eluted too close to the prominent peak *A*.

The relative percentages of the five Me esters showed minor variations in different samples. A tentative average attribution indicates: methyl pimarate 30 ± 3%, methyl sandaracopimarate 2%, methyl isopimarate 3%, methyl dehydroabietate 30 ± 3%, methyl abietate 35 ± 3%, calculated for the total content of diterpenic acids.

## EXPERIMENTAL

*Column chromatography.* Silica gel (0·06–0·20 mm). TLC: kiesel gel G. UV: EtOH soln. IR: Nujol mull. NMR: 60 MHz. $CDCl_3$ soln, TMS as internal standard. GLC: FID instrument, $N_2$ flow rate 20 ml/min, columns packed with (1) 3% SE-30 on Varaport 30, 100/120 mesh, 1·5 m × 3 mm, isothermal 220° (2) 5% Apiezon L on Chromosorb W AW/DMCS, 80/100 mesh, 1·5 m × 3 mm, isothermal 230° (3) 5% Carbowax 20 M on Chromosorb W AW/DMCS, 80/100 mesh, 3 m × 3 mm, isothermal 200° (4) 4% QF-1 on Chromosorb W DMCS, 60/80 mesh, 1·5 m × 3 mm, programmed 140–230° at 6°/min (5) 1% GE XE-60 on Chromosorb W AW/DMCS, 80/100 mesh, 1·5 m × 3 mm, programmed 140–230° at 6°/min. GC–MS: He flow rate 20 ml/min, 2 m column packed with 3% SE-20 on Chromosorb W 60/80 mesh.

*Origin of the resin.* Dragon's blood A-type resin was an authentic commercial sample. Samples of the resin purchased at different times had the same contents of diterpenic acids (qualitative and quantitative) and of flavonoid products.[4]

*Extraction and separation.* Finely powdered resin (100 g) was extracted in a Soxhlet with cyclohexane, yielding 55 g of a red, sticky gum. This material was adsorbed on silica gel (100 g) and introduced on top of a column packed with silica gel (900 g) in cyclohexane; for elution, cyclohexane, $C_6H_6$, $C_6H_6$–$Et_2O$ and EtOAc were used. The middle $C_6H_6$ fraction gave 8 g of a yellowish gum containing most of the resin acids. The gum (8 g) was chromatographed on silica gel (800 g); the $C_6H_6$–$Et_2O$ (4:1) eluate yielded 4 g of a white resin containing most of the resin acids. The chromatographic elutions were monitored by TLC and GLC (the samples were methylated with $CH_2N_2$ and tested against Me abietate). The white resin obtained was soluble in alkali; its IR spectrum showed a carboxyl stretching band at 1700 $cm^{-1}$. The MS had a $M^+$ peaks at *m/e* 300 and 302. The UV spectrum showed a main absorption pattern at 250, 241 and 234 nm, consistent with the occurrence of abietic acid, and a minor absorption at 276 and 267 nm, indicative of dehydroabietic acid. The resin was methylated with $CH_2N_2$ and purified on silica gel (250 g) and eluting with cyclohexane and then with $C_6H_6$. The most pure sample (1 g) arose from the middle cyclohexane fraction, some less pure product remaining in the other cyclohexane and $C_6H_6$ fractions. The oily mixture of Me esters had IR and UV spectra similar to those of the unmethylated

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[6] Nestler, F. H. M. and Zinkel, D. F. (1967) *Anal. Chem.* **39**, 1118.

[7] von Rudloff, E. and Sato, A. (1963) *Can. J. Chem.* **41**, 2165.

[8] Zinkel, D. F., Zank, L. C. and Wesolowski, M. F. (1971) *Diterpene Resin Acids*, U.S. Dept. of Agricult., Forest Service. Forest Products Laboratory, Madison.

material. The MS showed $M^+$ peaks at *m/e* 314 and 316. The NMR spectrum had many signals in the $\delta$ 0·90–1·30 region (C–Me), at least four signals around $\delta$ 3·60–3·70 (COOMe) and unresolved signals in the $\delta$ 5·00–7·00 range (olefinic and aromatic protons).

The resin content is estimated at about 3–6% by weight of the original "dragon's blood" resin.

*GC–MS. Compound* A. Prominent peaks at *m/e* 316, 301, 257, 241, 181, 180, 121: see [9–11] and MS of Me pimarate.[8] *Compound* C. Peaks at *m/e* 316, 301, 287, 257, 256, 242, 241, 148, 133, 121, 105, 81: see [9,11] and MS of Me isopimarate.[8] *Compound* D. Peaks at *m/e* 314, 299, 255, 240, 239, 197: see [9,12] and MS of Me dehydroabietate.[8] *Compound* E. Peaks at *m/e* 316, 301, 273, 256, 241, 213, 185, 136, 121, 105, 91: see [9] and MS of Me abietate.[8] For the discussion on the fragmentation pattern, we referred to [8–12].

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[9] Chang, T.-L., Mead, T. E. and Zinkel, D. F. (1971) *J. Am. Oil Chemists' Soc.* **48,** 455.

[10] Audier, H. E., Bory, S., Fétizon, M. and Anh, N.-T. (1966) *Bull. Soc. Chim. Fr.* 4002.

[11] Church, R. F. and Ireland, R. E. (1963) *J. Org. Chem.* **28,** 17.

[12] Enzell, C. R. and Wahlberg, I. (1969) *Acta Chem. Scand.* **23,** 871.