Phytochemistry, 1978, Vol 17, p 327 Pergamon Press. Printed in England

5α,8α-EPIDIOXY-5α-ERGOSTA-6,22-DIENE-3β-OL FROM *USNEA ANNULATA* AND *DACTYLINA ARCTICA*

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(*Revised received* 31 *May* 1977)

Key Word Index—*Usnea annulata*; *Dactylina arctica*; Usneaceae; lichens; sterol; 5α,8α-epidioxy-5α-ergosta-6, 22-diene-3β-ol.

INTRODUCTION

Previous work has described the presence of (+)-usnic acid in *Usnea annulata* [1] and usnic and gyrophoric acids in *Dactylina arctica* [1, 2].

RESULTS

Usnea annulata (Mull. Arg.) Tomin. (Voucher specimen in the herbarium of the Institute of Biology and Pedology, Far East Science Centre, USSR Academy of Sciences, Vladivostock, USSR) was collected from the Kamenushka River valley near Ussuriisk, Primorye Territory, USSR. The residue obtained after separation of (+)-usnic acid [1] and saponification with 5% NaOH was chromatographed on a Si gel (150–175 mesh) column. Elution with pentane–$CHCl_3$ (2:1) yielded a crystalline compound (0.026%), which after additional chromatography on a Si gel (175–200 mesh) column and recrystallisation had mp 178.5–180° (hexane), $C_{28}H_{44}O_3$ M^+ at *m/e* 428), $[\alpha]_D^{22}$ $-22.5°$ ($CHCl_3$), IR (KBr) cm^{-1}: 3540, 3420, 1380, 1050, 975, PMR ($CDCl_3$): δ 0.81–1.04 (18H), 3.96 (1H, *m*), 5.15–5.22 (2H, *m*), 6.35 (2H, AB-*q*, δ_{AB} 25 Hz, J_{AB} = 8.4 Hz) and was identical (TLC, mp, IR, PMR, MS, mmp) with the authentic sample of 5α,8α-epidioxy-5α-ergosta-6,22-diene-3β-ol [3].

Dactylina arctica (Hook) Nyl. was obtained from the upper reaches of Kolyma River near Kulu, Magadan Region, USSR. The residue obtained after separation of (+)-usnic acid [1] and evaporation of the solvent was chromatographed on Si gel (65–80 mesh). Elution with petrol (bp 70–100°)–$CHCl_3$ (1:1) yielded a crystalline product (0.027%) which, after additional purification (as described above), proved to be identical with 5α,8α-epidioxy-5α-ergosta-6,22-diene-3β-ol.

Acknowledgements—The authors thank L.A. Knyazheva (Department of Botany, Far East State University, Vladivostok) and Yu. B. Korolev (Institute of Biological Problems of the North, Far East Science Centre, USSR Academy of Sciences, Magadan) for identification of lichens.

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Phytochemistry, 1978, Vol. 17, pp. 327–328 Pergamon Press Printed in England.

1H-INDENE-2,3-DIHYDRO-4-CARBOXALDEHYDE AND 1H-INDENE-2,3-DIHYDRO-5-CARBOXALDEHYDE FROM THE SEEDS OF *AMOMUM MEDIUM*

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(*Revised received* 20 *August* 1977)

Key Word Index—*Amomum medium*; Zingiberaceae; 1H-indene-2,3-dihydro-4-carboxaldehyde; 1H-indene-2,3-dihydro-5-carboxaldehyde; seeds.

In a previous paper [1], we described the pharmacognostic properties of the seeds of *Amomum medium* Loureiro (*A. tsao-ko* Crevostet et Lemair*, ovoid China Cardamon†, commercially available in Japan and Hong Kong), one of the plant drugs of Chinese medicine. This report deals with the isolation and structural elucidation of two simple aldehydes along with α-pinene, β-pinene, myrcene, α-phellandrene,

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*Scientific Publish Academy (1976 in Peking) *Iconographia Cormophytorum Sinicorum* 5, 593.

†Smith F. P. (1969 in Taipai) *Chinese Materia Medica* (Rev. G. A. Stuart) 37.

limonene, 1,8-cineol and *p*-cymene in the volatile oil and ether extracts from this material.

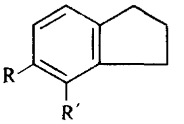
The ether extracts (20 ml) of the seeds (3 kg) were chromatographed on Si_2O with hexane–C_6H_6 mixtures (19:1–1:19) and C_6H_6 and analysed by TLC (Si gel GF (Merk), C_6H_6). The positive fractions with Brady's reagent were rechromatographed with C_6H_6 to give similar smelling, pale yellow oils **1** (25 mg) and **2** (20 mg). Analytical samples were obtained by prep TLC (Si gel GF (Merck), hexane). These compounds analysed for $C_{10}H_{10}O$. $M^+ = 146$ and preliminary investigation showed the presence of a CHO.

1 formed a 2,4-dinitrophenylhydrazone, orange needles, mp 253–254°, $C_{10}H_{14}N_4O_4$, $M^+ = 326.1006$. IR of **1** showed absorption at 1692 cm^{-1} due to the aromatic aldehyde. The PMR (60 M Hz) in CCl_4 showed signals at δ 2.19 (2H, *m*, CH_2), δ 2.98 (4H, *t*, $J = 8$ Hz, $CH_2 \times 2$), δ 7.12 (1H, *d*, $J = 10$ Hz, aromatic H), δ 7.52 (1H, *d*, $J = 10$ Hz, aromatic H), δ 7.59 (1H, *s*, aromatic H) and δ 9.82 (1H, *s*, aromatic CHO), suggesting that **1** contained three methylene groups, two aromatic *ortho* coupled protons, one isolated aromatic proton and an aromatic aldehyde.

Finally, the structure of **1** was established as 1H-indene-2,3-dihydro-5-carboxaldehyde by the agreement of IR and PMR with the published spectra [2,3].

Compound **2** also formed a 2,4-dinitrophenylhydrazone, orange needles, mp 259–260°, $C_{10}H_{14}N_4O_4$, $M^+ = 326.1023$. The IR of **2** showed absorption at 1700 cm^{-1} due to the aromatic aldehyde. The PMR in CCl_4, showed signals at δ 2.12 (2H, *m*, CH_2), δ 2.82 (2H, *t*, $J = 8$ Hz, CH_2), δ 3.16 (2H, *t*, $J = 8$ Hz, CH_2), δ 7.31 (3H, *m*, aromatic H) and δ 10.2 (1H, *s*, aromatic CHO), suggesting that **2** is an isomer of **1**.

2 therefore must be 1H-indene-2,3-dihydro-4-carboxaldehyde. Although previously synthesized [4], neither of these two aldehydes have been reported before as natural products.



1 : R = CHO, R' = H
2 : R = H, R' = CHO

Acknowledgements—The authors thank Miss Y. Kimura for IR and PMR and Mr. M. Aimi for MS

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Phytochemistry 1978, Vol 17, pp 328–329 Pergamon Press Printed in England

AEGELINOL, A MINOR LACTONIC CONSTITUENT OF *AEGLE MARMELOS*

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(*Received* 29 *July* 1977)

Key Word Index—*Aegle marmelos*; Rutaceae; aegelinol; 3'-epimer of decursinol

INTRODUCTION

A number of coumarins [1–6], alkaloids [1–3, 6–8], sterols [3, 4, 9] and essential oils [10] have been reported in *Aegle marmelos*. In the course of the present work a new coumarin, aegelinol, has been isolated from the root and stem-bark.

RESULTS AND DISCUSSION

Aegelinol shows the UV absorption of a 2',2'-dimethylchromeno-3'-hydroxycoumarin (λ_{max}^{EtOH} 336 nm; log ε 4.47; $\lambda_{max}^{EtOH+alkali}$ 320 nm; log ε 4.55). Strong absorptions at 3400 cm^{-1} (–OH) and 1720 cm^{-1} which indicate a lactone carbonyl, were discernible in the IR spectrum (nujol mull). In its 60 MHz NMR spectrum ($CDCl_3$) characteristic signals were observed for a gem-dimethyl group (δ 1.42, 6H, *s*), an alcoholic hydroxyl function (δ 2.51, 1H, *br* signal, disappeared on deuteration), a-C$\underline{H}_2$-C$\underline{H}$-system (δ 3.04, 1H, *d*, $J = 2.5$ Hz and δ 2.95, 1H, *d*, $J = 9.0$ Hz; δ 3.94, 1H, *m*), two aromatic para protons (δ 6.77 and 7.20, 1H, *s*, each) and the C-3 and C-4 protons of the coumarin nucleus (δ 6.20 and 7.60, 1H, *d*, each; $J = 9.5$ Hz). The secondary nature of the hydroxyl function (—CH—OH) was apparent from the downfield shift of the methine signal to δ 5.10 in aegelinol monoacetate, $C_{14}H_{13}O_3$. OCOMe, mp 138°. On dehydration with *p*-toluenesulphonic acid the compound afforded anhydromarmesin (**1**).

From the above data and from the mass fragmentation [*m/e* 264 (M^+), 217, 213, 188, 187, 160, 131, 119, 91 and