Phytochemistry, Vol. 27, No. 12, pp. 4000–4001, 1988.
Printed in Great Britain.

0031–9422/88 $3.00 + 0.00
Pergamon Press plc.

DORIASENINE, A PYRROLIZIDINE ALKALOID FROM *SENECIO DORIA*

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(*Received* 3 *May* 1988)

Key Word Index—*Senecio doria*; Asteraceae; pyrrolizidine alkaloids; doriasenine.

Abstract—A new pyrrolizidine alkaloid has been isolated from *Senecio doria* L. The structure was elucidated by IR, ^{1}H, ^{13}C NMR and mass spectroscopy. The name doriasenine is proposed.

INTRODUCTION

Plants containing pyrrolizidine alkaloids are of world-wide distribution. The most important genera are *Senecio* (Asteraceae) *Crotalaria* (Fabae), *Symphytum* and *Heliotropium* (Boraginaceae) [1, 2]. *Senecio doria* L., widely distributed in Spain, Austria, southern France, Hungary and Romania [3], belongs to the tribe Senecioneae, which is part of the family of the Asteraceae.

An alkaloid of the retronecine-type was isolated from this by Constantinesco and Albulesco [4] and we have now isolated a new pyrrolizidine alkaloid from this plant. Structural analysis was carried out by IR, ^{1}H, ^{13}C NMR and mass spectroscopy. The name doriasenine is proposed for this new alkaloid.

RESULTS AND DISCUSSION

The residue of the methanolic extraction of plant material was purified by DCC-chromatography in ascending mode [5]. The resulting IR data shows a hydroxyl, two ester groups and an asymmetrical substituted double bond. In the high resolution mass spectrum, the molecular peak at m/z 351 can be related to the molecular formula $C_{18}H_{25}NO_6$. The fragment $C_5H_6O_2$ (m/z 253) shows that the present pyrrolizidine alkaloid is an open-chain diester with an unsaturated, hydroxylated, C_5-carboxylic acid in position 9 as well as in position 7. The ^{1}H NMR-spectrum makes this evident by the signals at 6.33 and 5.88 ppm for an olefinic proton each.

The signal at 6.33 ppm is a quartet with a vicinal coupling of $J = 7$ Hz and the signal at 5.88 ppm forms a quartet with $J = 1$ Hz. The methyl-protons belonging to them appear at 1.97 and 2.0 ppm respectively. These values indicate the presence of β-hydroxy-angelic acid and γ-hydroxy-senecioinic acid. This is confirmed by the ^{13}C-signals at 140.54 (C-17) and 15.75 ppm (C-18) as well as 112.89 (C-11) and 15.59 ppm (C-14). The position of the esterifications can be cleared up by the MS-decay.

Because of the double bonding between C-1 and C-2 the ion collision induced fragmentation has to begin at position 9. The intensive ion m/z 253 proves that C-9 is esterified with β-hydroxy-angelic acid. The m/z 253 can develop after a rearrangement and ester splitting. Elimination of another OH-leads to the ion m/z 236.

At C-7 γ-hydroxy-senecioinic acid is present, as the less intensive ion m/z 235 proves, which developed by the elimination of $C_5H_8O_3$ after a McLafferty-rearrangement. This MS-decay is shown in Figs 1 and 2. The MS-fragmentation between m/z 138 and 80 indicates that for the necine, only retronecine and heliotridine is possible. The signal at 2.62 ppm for C-6-H_2 in the ^{1}H NMR spectrum proves that here retronecine is present [6].

All peak-values were verified by decoupling experiments and interpretation of the off-resonance and coupled spectra respectively. After interpretation of all data (Tables 1 and 2), the alkaloid is identified as a 7-γ-hydroxy-senecioyl-9-β-hydroxy-angeloyl-retronecine The alkaloidal content is found to be 0.25–0.35%.

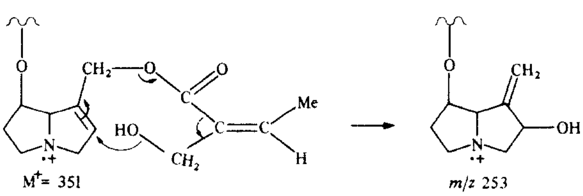


Fig. 1. Rearrangement and ester splitting to m/z 253.

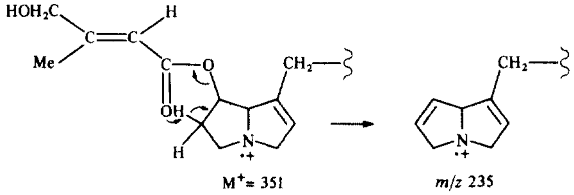


Fig. 2. McLafferty-rearrangement to m/z 235.

Table 1. ^{1}H NMR data of **1**

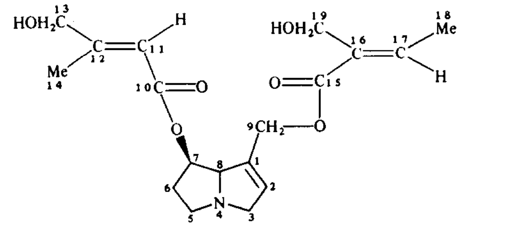
H	
17	6.33, 2H, *q*, $J = 7$
11	5.88, 1H, *q*, $J = 1$
2	5.76, 1H, *m*
7	5.34, 1H, *t*, $J = 5$
9	4.71, 2H, *br s*
13	4.57, OH, *s*
19	4.57, OH, *s*
8	4.29, H, *m*
19	4.17, 2H, *s*
13	4.03, 2H, *s*
3	3.82, 2H, *m*
5	3.33, 2H, *m*
6	2.62, 2H, *m*
14	2.00, 3H, *d*, $J = 1$
18	1.97, 3H, *d*, $J = 7$

δ-Values in ppm; J in Hz.

Table 2. ^{13}C NMR data of **1**

C		C	
18	15.73	8	75.67
14	15.79	11	112.89
6	34.34	2	127.30
5	53.60	12	131.76
9	60.56	1	133.67
3	62.27	17	140.54
19	64.25	16	159.57
13	66.67	15	165.98
7	73.05	10	166.57

δ-Values in ppm.



Doriasenine (**1**)

EXPERIMENTAL

Senecio doria L. was collected near Budapest, Hungary, and Sibiu, Romania. The dried and pulverized drug was extracted with MeOH in a Soxhlet apparatus. After evapg to dryness the resulting residue was dissolved in 2.5% HCl and extracted with Et_2O. The aq. phase was basified with NH_3 (25%) and extracted with CH_2Cl_2. The solvent of the organic phase was removed under red. pres. The solid yellow residue was purified by countercurrent chromatography in ascending mode. Liquid phase: $CHCl_3$, $C_6H_5CH_3$, MeOH, H_2O (5:5:7:2). The spectra were recorded as follows: NMR: ^{1}H: 90 MHz, ^{13}C: 22.63 MHz. Mass: MS 50, Cond. 70 eV, 180°. Doriasenine (**1**). Colourless oil (35 mg); $[\alpha]_D^{20}$ +6° (EtOH), IR ν_{max}^{KBr} cm^{-1}: 1740–3400 (OH) (satd ester), 1710 (α,β-unsatd ester), 1650 (C=C). EIMS: m/z (% rel. int.): M^+ calc.: $C_{18}H_{25}NO_6$: 351, 1675; found: 351, 1680 (8, 7), 254 (5, 6), 253, 1323 (36, 4) = $C_{15}H_{19}NO_4$, 252 (7, 4) 236 (21, 2), 235, 1206 (17, 3) = $C_{13}H_{17}NO_3$, 209 (9, 1), 155 (13, 1), 154 (16, 6), 151 (6, 2), 150 (11, 7), 139 (5, 5), 138 (27, 1), 137 (32, 8), 136 (76, 5), 135 (5, 4), 134 (11, 0), 126 (5, 4), 122 (18, 8), 121 (17, 0), 120 (36, 7), 119 (22, 4), 118 (8, 3), 117 (6, 4), 111 (7, 0), 108 (6, 3), 106 (11, 3), 99 (22, 9), 98 (15, 5), 97 (5, 1), 95 (11, 4), 94 (48, 7), 93 (100, 0), 87 (8, 3), 82 (5, 2), 80 (25, 3). ^{1}H NMR: see Table 1; ^{13}C NMR: see Table 2. $CDCl_3$; internal standard: TMS.

Acknowledgements—The authors are grateful to Dr H. Heltmann (Institut für Pharmazeutische Biologie der Universität Bonn) for collection and identification of the plant material.

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