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LACTONIC LIGNANS FROM *CNICUS BENEDICTUS*

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Key Word Index—*Cnicus benedictus*, Compositae, 2,3-dibenzylbutyrolactone lignans, nortracheloside, 2-acetylnortracheloside; trachelogenin; arctigenin

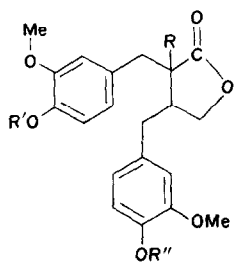
Plant. Cnicus benedictus L. identified at the Botanical Institute of the Free University of Brussels. *Source.* Jardin Expérimental J. Massart (Brussels). *Previous work.* Arctiin in fruit; none in other parts of the herb [1].

Present work. The dried and powdered herb (3·6 kg) was extracted with $CHCl_3$. Oils, waxes and chlorophyls were removed by eluting the extract on cellulose with H_2O–MeOH (4:1). After evaporation under reduced pressure, the H_2O–MeOH solution was purified by multiple dry-column chromatography on Si gel with $CHCl_3$–Me_2CO (4:3), to give two fractions: I, crude cnicin; and II, analytical TLC of II showed a complex mixture with 5 major spots detected by $I_2/CHCl_3$. Repetitive PLC on Si gel with CCl_4–Me_2CO (4:1 and 7:3) led to isolation of arctigenin (*A*; 15 mg), trachelogenin (*B*; 90 mg), nortracheloside (D_1; 60 mg), 2-acetylnortracheloside (D_2; 10 mg) and *C* which was earlier identified as salonitenolide [2].

Compounds *A*, *B*, D_1 and D_2 were characterized from their spectral (UV, IR, PMR, MS) properties, by chemical methods (methylation, acetylation, alkaline oxidation) and, for compounds *A* and *B*, direct comparison with authentic samples. As previously reported [1], no arctiin was detected

Examination of D_2. The compound D_2 has not been reported previously. MS (probe, direct inlet, 180°) 70 eV: 578 M^+ [5] ($C_{28}H_{34}O_{13}$), 536·1986 ($M^+ - 42$, Calc mass for $C_{26}H_{32}O_{12}$: 536·1891), 518·1863 ($M^+ - 42$; 18. Calc mass for $C_{26}H_{30}O_{11}$: 518·1787). 298·1194 ($M^+ - 42$; 30; 30; glucosyl. Calc mass for $C_{18}H_{18}O_4$: 298·1203) and 137·0599 (100) (Calc mass for $C_8H_9O_2$: 137·0602).

100 Mc PMR spectrum of D_2 in $CDCl_3$ is comparable to that of D_1, but a singlet was observed at δ 2·02 (3 H). The IR spectrum of D_2 in $CHCl_3$ (1740 cm^{-1} >C=O, in addition to 1780 cm^{-1} γ-lactone>C=O) also agreed with the presence of an aliphatic acetyl.



	R	R′	R″
(*A*) Arctigenin	H	H	Me
(*B*) Trachelogenin	OH	H	Me
(D_1) Nortracheloside	OH	Glc	H
(D_2) 2-Acetylnortracheloside	OAc	Glc	H

Treatment of D_2 with saturated Na_2CO_3 in MeOH gave D_1; hydrolysis of both compounds, D_1 and D_2, with 3 *N* H_2SO_4 afforded 2 non-identical genins and glucose identified by PC and GLC after silylation. Treatment of the genins with $POCl_3$ led for the genin from D_1 (nortrachelogenin) to a dehydration product with rupture at C-3/C-5 of the lignan (220 M^+, $C_{12}H_{12}O_4$). The genin from D_2 was not transformed under these conditions. These results unequivocally confirmed the position of the acetyl at C-2 of lignan D_2.

Studies are in progress to evaluate further the antibacterial and antitumoral potential of such compounds in *Cnicus benedictus*.

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