

inorganic salts by extraction of the residue twice with chloroform followed by evaporation of the solvent left an oil (1.7 g), which to over 95 % extent consisted of a mixture of trimethyl isocitrate and dimethyl isocitrate lactone in the approximate ratio 10:1 (NMR).

Trimethyl isocitrate: ^1H NMR, $\delta(\text{CDCl}_3)$: 4.39 (d, 1 H, $J=3$ Hz), 3.9–3.3 (11 H), 3.05–2.52 (2 H, AB part of ABX spectrum, $J_{AB}=17$ Hz, $J_{AX}=7$ Hz, $J_{BX}=8$ Hz).

(-)-Decylcitric acid. The ester obtained in the extraction with light petroleum was hydrolysed with sodium hydroxide solution (2 M, reflux overnight). After washing with ether and acidification, the decylcitric acid was extracted with ether. The ether solution was dried (Na_2SO_4) and concentrated, and the residue was recrystallised first from water and then from acetone-light petroleum affording (-)-decylcitric acid, m.p. 135–139 °C, $[\alpha]_{\text{D}}^{21}$ -21° (c 1.7, acetone). Lit.¹ value: $[\alpha]_{\text{D}}^{20}$ -10.9° (c 1.8, acetone).

Characterisation of (+)-isocitric acid. The mixture of trimethyl isocitrate and dimethyl isocitrate lactone obtained in the chloroform-ethanol extraction was distilled at 150 °C (0.3–0.4 kPa) giving dimethyl isocitrate lactone, free from trimethyl isocitrate (GLC). Recrystallisation from methanol gave a sample with m.p. 106–107 °C and $[\alpha]_{\text{D}}^{22}$ -65° (c 1.8, methanol). Lit.² m.p. 108.5–109 °C and lit.³ $[\alpha]_{\text{D}}$ -65° (methanol). ^1H NMR, $\delta(\text{CDCl}_3)$: 5.08 (d, 1 H, $J=8$ Hz), 3.9–3.5 (7 H, including two 3 H singlets at 3.78 and 3.74), 3.19–2.56 (AB part of an ABX spectrum, 2 H, $J_{AB}=17$ Hz, $J_{AX}=9$ Hz, $J_{BX}=9$ Hz).

Acknowledgements. We thank Mr. Lars Lindblom and Mr. Bengt Lindqvist for measuring the NMR spectra and the Swedish Natural Science Research Council for support.

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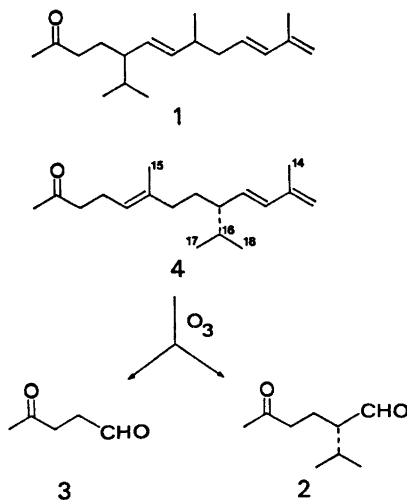
Received November 19, 1975.

Tobacco Chemistry 37. The Absolute Configuration of Prenylsolanone, (9S)-6,12-Dimethyl-9-isopropyltrideca-5E,10E,12-trien-2-one, a Nor-thunberganoid of *Nicotiana tabacum* L.

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Recent studies have revealed that both the tobacco diterpenoids of the thunbergane type and several of the tobacco volatiles which are structurally reminiscent of the thunberganoids, possess the same absolute configuration, *S*, at the carbon atom carrying the isopropyl group thus strengthening the hypothesis that such diterpenoids act as precursors of the smaller molecules.^{1–4} In the present communication we wish to report the chirality of another tobacco nor-thunberganoid, prenylsolanone.



In a preliminary report 8,12-dimethyl-5-isopropyltrideca-6,10,12-trien-2-one (*I*) was proposed⁵ as the structure of a new tobacco constituent isolated from the carbonyl fraction of the essential oil of *Nicotiana tabacum* L. The carbon skeleton of this ketone (*I*) indicated that it was a nor-thunberganoid and a determination of the chirality of the isopropyl-bearing carbon atom would throw further light on this question. Ozonolysis of the ketone furnished the expected ketoaldehyde, (2*S*)-5-oxo-2-isopropylhexanal (*2*), but the second product, 4-oxopentanal (*3*) was inconsistent

Table 1. ^{13}C chemical shifts and lanthanide-induced shifts (LIS) of prenylsolanone (4).

Carbon	Chemical shift ^a	LIS ^b
1	29.87	42.3
2	208.65	100.0
3	43.80	39.7
4	22.54	25.4
5	122.52	12.9
6	136.67	7.1
7	37.74	3.1
8	30.71	1.9
9	49.18	0.9
10	133.99	0.6
11	132.88	0.2
12	142.16	0
13	114.11	0.2
14	18.82	0.1
15	16.02	5.0
16	32.15	0.3
17	20.82	0.2
18	19.10	0.2

^a δ -values in ppm downfield from TMS. ^b Relative shifts induced by $\text{Yb}(\text{dpm})_3$. The effect ^c of "complex-formation shift" was not evaluated.

with the assumed constitution. Similarly, the ^{13}C NMR spectrum revealed two non-protonated olefinic carbons and the ^1H NMR spectrum showed five olefinic protons and two vinylic methyl groups (δ 1.83 and 1.59). These NMR data suggested that the structure tentatively proposed by Devreux and Beaulieu,⁵ 8,12-dimethyl-5-isopropyltrideca-6,10,12-trien-2-one (1) should be revised to 6,12-dimethyl-9-isopropyltrideca-5*E*,10*E*,12-trien-2-one (4) which also complies with the ozonolysis products. The ^{13}C chemical shifts of this compound (4) are given in Table 1 and the assignments, made by comparison of these data and those of structurally related compounds^{3,7} were confirmed with the aid of $\text{Yb}(\text{dpm})_3$ -induced shifts. The revised structure 4 is the same as that assigned to prenylsolanone which Demole and Enggist⁶ very recently reported as a constituent of Burley tobacco flavour. Direct comparison of our sample with synthetic prenylsolanone kindly provided by Dr. Demole confirmed the identity.

The present ozonolytic degradation to (2*S*)-5-oxo-2-isopropylhexanal (2) established the absolute configuration of prenylsolanone (2) as *S* in agreement with the chirality of other tobacco constituents assumed to be northuberganoids.¹⁻⁴ The optical activity of the ketoaldehyde 2 was somewhat lower than that previously reported² for this compound implying that the present prenylsolanone was partially racemic (enantiomeric ratio ca. 70:30), or that partial racemisation of the ketoaldehyde

2 had occurred during work-up. The present ^{13}C NMR results confirmed the *B*-configuration previously assigned to the 5,6-double bond ($\delta_{\text{C}(15)} = 16.02$; $\Delta\delta_{\text{C}(15)} > \Delta\delta_{\text{C}(7)}$).⁸

Experimental. IR spectra, rotations and mass spectra were recorded on Digilab FTS-14, Perkin-Elmer 141 and LKB 2091 instruments, respectively. Proton noise decoupled and single frequency off-resonance decoupled ^{13}C NMR and ^1H NMR spectra were obtained in CDCl_3 solutions in FT-mode on a Varian XL-100-12 spectrometer equipped with S-124 FT/disk accessories and controlled by a Varian 620 L computer. GC-MS was performed on a Varian 1700 chromatograph attached to the LKB 2091 instrument using glass capillary columns (5 m \times 0.25 mm) coated with Emulphor. The spectral data of the title compound were indistinguishable from those reported by Demole and Enggist⁶ for prenylsolanone. ^{13}C NMR data: see Table 1. $[\alpha]_D^{20} + 10.8^\circ$ (589 nm), $+ 11.5^\circ$ (578), $+ 13.6^\circ$ (546), $+ 27.6^\circ$ (436), $+ 53.1^\circ$ (365) (c 1.1; CHCl_3). The present compound did not separate from synthetic prenylsolanone when co-injected on a glass capillary column. Ozonolysis of prenylsolanone was performed as outlined previously³ furnishing 4-oxopentanal (3) and (2*S*)-5-oxo-2-isopropylhexanal (2) possessing spectral data identical with those previously published.³ The optical activity of the latter ketoaldehyde (2) was $[\alpha]_D^{20} + 17.4^\circ$ (589 nm), $+ 17.9^\circ$ (578), $+ 22.0^\circ$ (546), $+ 60.5^\circ$ (436), $+ 184.1^\circ$ (365) (c 0.39; CHCl_3); lit.² $[\alpha]_D^{20} + 47.8^\circ$ (589 nm), $+ 50.7^\circ$ (578), $+ 61.4^\circ$ (546), $+ 146.6^\circ$ (436), $+ 400.8^\circ$ (365) (c 0.73; CHCl_3).

Acknowledgements. The authors are indebted to Miss Ann-Marie Eklund for skilful technical assistance and Dr. Edouard Demole, Firmenich & Cie., Geneva, for a generous sample of prenylsolanone.

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Received November 14, 1975.