3,7,11,15-Cembratetraen-6-ol, a New Cembranoid from Tobacco, III

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3,7,11,15-Cembratetraene-6-ol (**1**) was isolated from tobacco and identified as a new natural product by spectral data and chemical degradation. 1-H-NMR, 13-C-NMR and MS data are given.

Leaves of *Nicotiana tabacum* are covered with a sticky execude containing only cembranoic or additionally labdanoic diterpenes, which are important flavour substances [1–3]. During investigation of cembranoid distribution of various tobaccos **1** was isolated and its structure proven by 1-H-NMR, 13-C-NMR, MS [4] and chemical degradation.

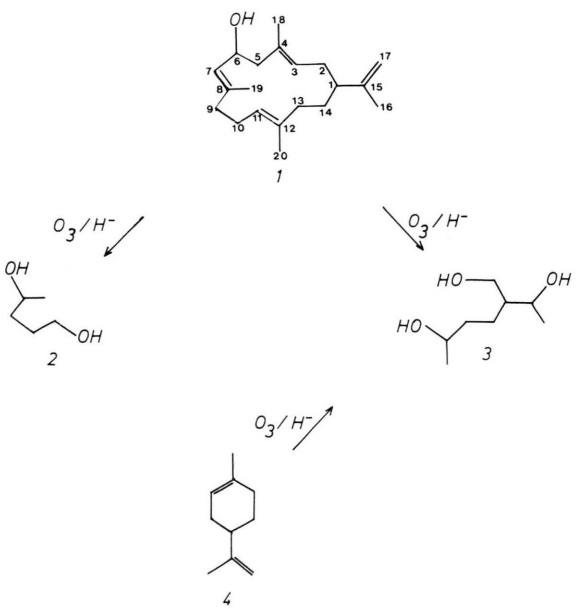
Oriental tobacco was extracted with liquid CO_2 and fractionated as described earlier [5]. A fraction enriched with cembranoids eluted from silicagel with petrolether/diethylether 75:25 (v:v) was separated further by repeated column chromatography and preparative TLC and led to isolation of **1**.

An analysis of the olefinic region in the 1-H-NMR spectrum established the presence of three trisubstituted ($\delta = 4.98$, 5.15 and 5.28) and one 1,1-disubstituted ($\delta = 4.61$ and 4.70) double bonds. The spectrum displays four signals for methylgroups attached to a tertiary sp2-carbon ($\delta = 1.55$, 1.60, 1.63 and 1.67) and one signal for a hydrogen attached to a carbon bearing a secondary, allylic oxygen ($\delta = 4.63$) which is consistent with 13-C data.

Since other data indicated the presence of a macrocyclic cembranoid compound **1** was degraded by ozonolysis followed by reduction with $NaBH_4$ yielding diol **2** and triol **3**. The structure of 1,4-pentandiol (**2**) was established by comparison with an authentic sample. The structure of 3-hydroxy-ethyl-heptandiol-2,6 was proved by comparison with the product of ozonolysis of limonene (**4**) followed by reduction.

The structure of degradation products **2** and **3** established the positions of double bonds at C-3, C-7, C-11 and C-15. Investigation of the signal in 1-H-NMR spectrum due to the secondary alcoholic group determined its position at C-6. The chirality at C-6 remains unknown.

As compound **1** can not be derived from cembrene or the main tobacco cembranoids α- and β-2,7,11-cembratriene-4,6-diol by simple oxidation-, rearrangement- or elimination reactions as all other tobacco cembranoids [3], we analyzed fresh surface gum. 3,7,11,15-Cembratetraene-6-ol was identified in surface gum of *N. tabacum* as well as in *N. sylvestris*.



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The new natural compound is the first identified tobacco cembranoid bearing an exocyclic double bond at C-15. The corresponding hydrocarbon, cembrene-A, is already identified in resinous plants, insects, and marine invertebrates [6]. In the soft coral *Sinularia flexibilis* cembrene-A is accompanied by the cyclopentadecatetraenic hydrocarbon flexibilene [7].

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[3] C. Enzell, I. Wahlberg, and A. Aasen, Progress Chem. Natural Products **35,** 1 (1977).
[4] MS (70 eV) (*m/z* (%)): 288 (M, 5.5), 270 ($M^{\cdot+}$-H_2O, 7), 255(8), 227(7), 187(8), 159(12), 147(14), 136(18), 119(46), 107(45), 93(92), 84(96), 81(100), 69(94), 55(64) 1-H-NMR($CDCl_3$): δ = 1.55(s)/1.60(s)/1.63(s)/1.67(s) (H-17/H-18/H-19/H-20), 2.17 (dd, J = 11.0 and −13.0 Hz, H-5a), 2.49 (broad d, J = 13 Hz, H-5b), 4.61 (dd, J = 0.7 and 2.4 Hz, H-16a), 4.63 (ddd, J = 3.8, 9.2 and 11.0 Hz, H-6), 4.70 (dd, J = 2.4 and 1.4 Hz), 4.98 (broad t, H-11), 5.15 (d, J = 9.2 Hz, H-7), 5.28 (t, J = 7.8 Hz, H-3) 13-C-NMR($CDCl_3$): δ = 15.5(q)/16.4(q)/18.6(q)/19.0(q) (C-16/C-18/C-19/C-20), 23.5 (t, C-10), 27.7 (t, C-14), 32.8 (t, C-2), 33.6 (t, C-13), 33.6 (t, C-13), 39.4 (t, C-9), 45.9 (d, C-1), 47.8 (t, C-5), 66.7 (d, C-6), 110.4 (t, C-16), 120.5 (d, C-3), 125.2 (d, C-11), 129.0 (d, C-2), 132.4 (s, C-12), 134.2 (s, C-4), 138.7 (s, C-8), 149.1 (s, C-15).
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