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Tobacco Chemistry. 44. (1*S*,2*E*,4*R*,6*E*,8*R*,11*S*,12*R*)- and (1*S*,2*E*,4*S*,6*E*,8*R*,11*S*,12*R*)-8,11-Epoxy-2,6-thunbergadiene-4,12-diol. Two New Diterpenoids of Greek Tobacco

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Two new diterpenoids were isolated from Greek *Nicotiana tabacum* L. One of them was shown to be (1*S*,2*E*,4*S*,6*E*,8*R*,11*S*,12*R*)-8,11-epoxy-2,6-thunbergadiene-4,12-diol (*1*) by synthesis and X-ray analysis, while the other was tentatively assigned the structure (1*S*,2*E*,4*R*,6*E*,8*R*,11*S*,12*R*)-8,11-epoxy-2,6-thunbergadiene-4,12-diol (*2*) by spectroscopic means. The implication of these results on the biogenesis of the tobacco thunberganoids is discussed.

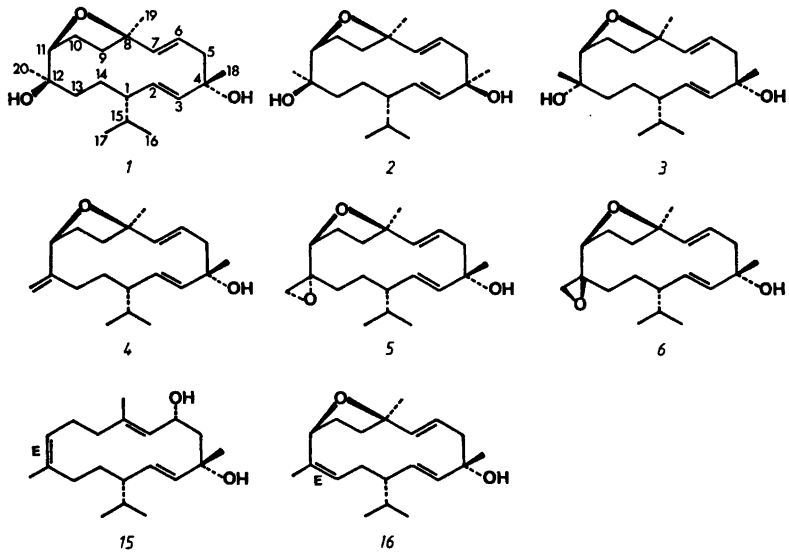
Carotenoids, labdanoids and thunberganoids are important precursors of a large number of the volatile odoriferous constituents of tobacco.[1] A knowledge of the structures of the precursors is of vital importance for the understanding of the mechanisms involved in the formation of the degradation products, and this has stimulated thorough chemical studies on the diterpenoids of tobacco.[1–7] The present communication describes the isolation and structure elucidation of two new diterpenoids (*1*, *2*) of the thunbergane type isolated from Greek tobacco.

RESULTS

Both tobacco isolates (*1*, *2*) had the composition $C_{20}H_{34}O_3$ and exhibited similar spectral properties. An analysis of these spectral data, which will be given below for compound *2*, led to a tentative assignment of compound *1* as a (2*E*,6*E*)-8,11-epoxy-2,6-thunbergadiene-4,12-diol.

In order to confirm this the (1*S*,2*E*,4*S*,6*E*,8*R*,11*S*)-8,11-epoxy-2,6-thunbergadiene-4,12-diols *1* and *3*, epimeric at C-12, were prepared. Thus, (1*S*,2*E*,4*S*,6*E*,8*R*,11*S*)-8,11-epoxy-2,6,12(20)-thunbergatrien-4-ol (*4*) was converted by selective oxidation to the C-12-epimeric 1,2-epoxides, the least polar of which (*5*) gave a ^{1}H NMR spectrum containing a two-proton singlet at δ 2.68, assigned to the protons at C-20; the spectrum of the more polar epoxide (*6*) exhibited the H-20a and H-20b doublets at δ 2.48 and 2.80. Reduction of these epoxides (*5*, *6*) using LAH afforded the two 4*S*-diols *3* and *1* respectively. One of these (*1*) was identical in all respects ($[\alpha]_D$, IR, NMR, MS) to diol *1* of tobacco, a result which determined the structure and stereochemistry at all centers except for C-12. Since the chirality at this center could not be assigned unambiguously by spectroscopic means, a single crystal X-ray analysis of the tobacco diol *1* was undertaken.

Diol *1* crystallizes in the tetragonal space group $P4_3$ with two molecules in the asymmetric unit, $a = 11.073$ (3), $b = 11.073$ (3) and $c = 34.102$ (13) Å. Intensity data were collected on the Philips computer-controlled PW 1100 diffractometer. An *E* map with structure-factor phases determined by direct methods displayed 30 of the 46 non-hydrogen atoms of the two independent molecules. The missing



non-hydrogen atoms were located from a difference Fourier synthesis. The present R value after two cycles of anisotropic refinement including all non-hydrogen atoms is 0.12. A stereoscopic view of diol *1*, summarising the X-ray results to be discussed in detail elsewhere, is given in Fig. 1. It followed from these results that diols *1* and *3* have 12R- and 12S-configuration, respectively.

The ^{13}C NMR spectrum of the second tobacco isolate (*2*) confirmed the presence of twenty carbon atoms and single-frequency off-resonance decoupling demonstrated that these comprise five methyl groups, five sp^3 methylene groups, three sp^3 methine groups, one of which carried an oxygen atom, four sp^2 methine groups and three fully substituted, oxygen-carrying sp^3 carbon atoms. The ^{1}H NMR spectrum of *2* displayed methyl doublets at δ 0.85 ($J = 6$ Hz) and 0.89 ($J = 6$ Hz) and the IR spectrum bands at 1375 and 1385 cm^{-1}, which indicated that two of the methyl groups formed part of an isopropyl group. The remaining three methyl groups, giving rise to three-proton

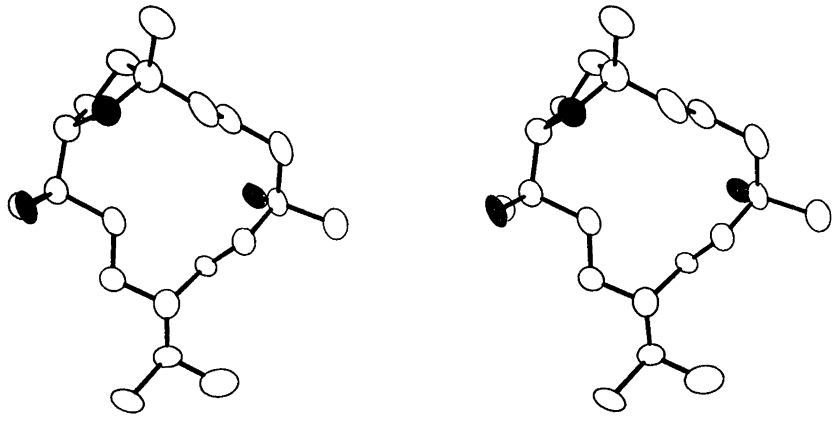


Fig. 1. Stereoscopic view of (1S,2E,4S,6E,8R,11S,12R)-8,11-epoxy-2,6-thunbergadiene-4,12-diol (*1*, oxygen atoms shaded).

Table 1. Carbon-13 chemical shifts and assignments for compounds *1* – *4* and *16*.[a]

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15	C-16/C-17	C-18	C-19	C-20
1	50.9	129.4	138.2	73.6	45.6	122.6	139.6	82.9	35.1	27.0	88.9	74.1	36.7	28.5	32.3	20.7/20.0	30.1	29.2	22.1
2	50.9	132.2	137.4	73.3	46.7	121.5	140.1	83.0	34.6	25.7	89.0	74.2	36.0	28.5	31.9	20.7/20.4	24.8	29.1	21.8
3	51.4	130.1	138.3	73.4	45.2	123.1	140.0	83.5	34.0	25.4	87.5	74.8	36.2	26.8	32.4	20.9/19.8	30.1	29.5	24.8
4	50.5	129.1	138.4	73.6	45.3	122.2	139.5	83.1	34.1	31.7	86.0	149.8	36.2	27.2	32.1	20.7/19.7	30.4	28.8	113.6
16	50.0	129.5	138.5	73.7	45.5	123.4	140.0	83.1	34.3	30.9	82.4	134.6	122.2	29.5	32.3	20.7/19.2	29.5	28.7	14.3

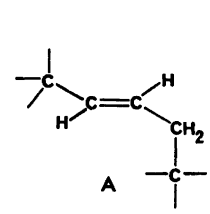
[a] δ-Values relative to TMS.

singlets at δ 0.99, 1.31 and 1.35 in the ^{1}H NMR spectrum must hence be attached to the fully substituted oxygen-carrying carbon atoms.

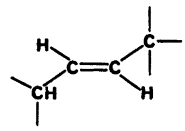
The ^{1}H NMR spectrum of *2*, exhibiting signals due to four protons in the olefinic region and a one-proton multiplet at δ 3.97, also confirmed the presence of the two disubstituted double bonds, and the oxygen-carrying methine carbon. Moreover, it followed from the ^{13}C chemical shift value, 89.0 ppm (*cf.* Table 1, which for comparison purposes also includes data for compounds *1*, *3*, *4* and *16*), and the observation that *2* did not undergo acetylation under standard conditions (Ac_2O/pyridine) that this methine carbon is linked to an ether oxygen. This view was supported by the fact that compound *2* incorporates four oxygen-bearing carbons and only three oxygens. Since the IR spectrum showed absorption at 3430 cm^{-1} and was devoid of carbonyl absorption, it was evident that the remaining two oxygens are present as tertiary hydroxyl groups. The properties of diol *2* are thus markedly similar to those of (1*S*,2*E*,4*S*,6*E*,8*R*,11*S*,12*R*)-8,11-epoxy-2,6-thunbergadiene-4,12-diol (*1*) and it appeared likely that the two compounds were structurally closely related.

This view was corroborated by ^{1}H NMR experiments. Thus, spin decoupling, spin tickling and spin simulation experiments and solvent shift observations established that the two disubstituted double bonds in diol *2* have *E*-configurations and clarified the nature of the adjacent carbons. One of the double bonds has a fully substituted carbon geminal to one of its olefinic protons (δ 5.47, d, $J = 15.6$ Hz) and a methylene group (δ 2.29, d, $J = 6.5$ Hz), which in turn is adjacent to a non-protonated carbon, geminal to the other olefinic proton (δ 5.32, dt, $J = 15.6$ and 6.5 Hz), *i.e.* diol *2* incorporates unit A. The protons of the second olefinic unit (δ 5.40, d, $J = 15.6$ Hz and δ 5.11, dd, $J = 15.6$ and 8.7 Hz) are geminal to a fully substituted carbon and a methine group (δ 2.0), respectively, unit B.

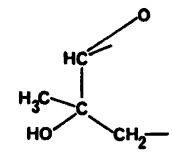
Although LIS experiments were complicated due to the different complexing ability of the three oxygen atoms, additional support for the structure of diol *2* could be obtained when the three methyl singlets at δ 0.99, 1.31 and 1.35 were used as monitoring peaks. Thus, the largest downfield shifts on addition of Eu(dpm)$_3$,



A



B



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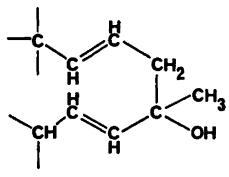
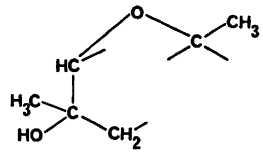
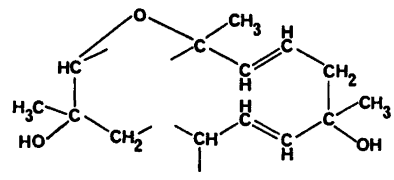


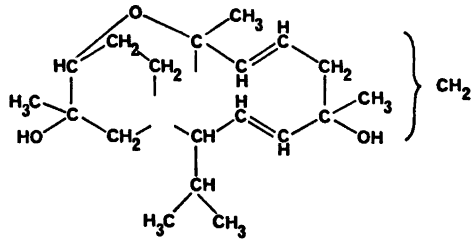
D



E



F



G

$\Delta = 180$ Hz,* were found for the methyl singlet at δ 0.99, the one-proton multiplet at δ 3.97 and a one-proton multiplet of the methylene envelope; the last signal corresponds to a proton on one of the methylene groups, which carries non-equivalent protons. These results suggest that diol *2* incorporates unit C.

Downfield shifts of intermediate magnitude, $\Delta = 115$ Hz, were observed for the methyl singlet at δ 1.31, the allylic methylene signal at δ 2.29 and the four olefinic proton signals. These data allowed the moulding of units A and B to partial structure D.

The smallest downfield shift was found for the methyl singlet at δ 1.35, $\Delta = 40$ Hz, which indicates that the corresponding methyl group is geminal to the ether oxygen. Unit C could thus be extended to unit E, which could only be combined with D as shown in partial structure F.

With this information at hand it followed from simple chemical shift calculations [8] that the methine carbon of the isopropyl group resonating at δ 31.9, must be linked to the methine group which gives rise to the proton signal at δ 2.0.

This left three methylene groups to be accounted for. Since the one-proton signal at δ 3.97 showed a second-order splitting interpretable in terms of virtual spin-spin coupling, it was evident that two of these methylene groups were adjacent to the secondary ether carbon, giving partial structure G.

Insertion of the remaining methylene group and closure of the rings could be made in different ways giving several alternative structures. These could not be differentiated by chemical means, since there was only a very limited amount of diol *2* available, and no appropriate starting material for synthesis.

* Spectra were recorded of samples containing three incremental concentrations of shift reagent. The induced shifts, Δ, were measured in the spectrum of the sample having the highest concentration of shift reagent; the exact molar ratio of substrate/reagent was not determined.

However, a comparison of the ^{13}C NMR spectrum of diol *2* with those of (1*S*,2*E*,4*S*,6*E*,8*R*,11*S*,12*R*)- and (1*S*,2*E*,4*S*,6*E*,8*R*,11*S*,12*S*)-8,11-epoxy-2,6-thunbergadiene-4,12-diol (*1* and *3*) proved fruitful and actually suggested that (2*E*,6*E*)-8,11-epoxy-2,6-thunbergadiene-4,12-diol was the most reasonable structure of diol *2*. Moreover, since the signals assigned to C-1, C-8, C-11 and C-19 were present at virtually invariant positions in the spectra of diol *2* and the 1*S*,8*R*,11*S*-derivatives *1* and *3*, diol *2* was provisionally identified as one of the two (1*S*,4*R*,8*R*,11*S*)-4,12-diols.

The 4*R*-configuration was substantiated by comparison of the ^{13}C NMR data for the diols *1*, *2* and *3*. Thus, the resonances ascribed to C-5 and C-18 were positioned at δ 45.6 and 30.1 and at δ 45.2 and 30.1 in the spectra of the 4*S*-diols *1* and *3* respectively, while the corresponding resonances for *2* appeared at δ 46.7 and 24.8.

The configuration at the remaining asymmetric center, C-12, in diol *2*, deduced to be *R*, also rested on NMR evidence. The C-20 signals were present at virtually invariant positions, δ 22.1 and 21.8, in the ^{13}C NMR spectra of the 12*R*-diol *1* and diol *2*, whereas that of the 12*S*-diol (*3*) was found at δ 24.8. Moreover, the 12*R*- and 12*S*-diols (*1*, *3*) exhibited the three-proton singlet due to the methyl group at C-12 (H-20) at δ 1.02 and 1.10. The corresponding signal for diol *2* appeared at δ 0.99, a result which is in harmony with a 12*R*-configuration.

We therefore propose that diol *2* can be formulated as (1*S*,2*E*,4*R*,6*E*,8*R*,11*S*,12*R*)-8,11-epoxy-2,6-thunbergadiene-4,12-diol, *i.e.* it differs from diol *1*, (1*S*,2*E*,4*S*,6*E*,8*R*,11*S*,12*R*)-8,11-epoxy-2,6-thunbergadiene-4,12-diol, with respect to the configuration at C-4. This result is in agreement with the fact that thunberganoids epimeric at this center are commonly encountered in tobacco.[1]

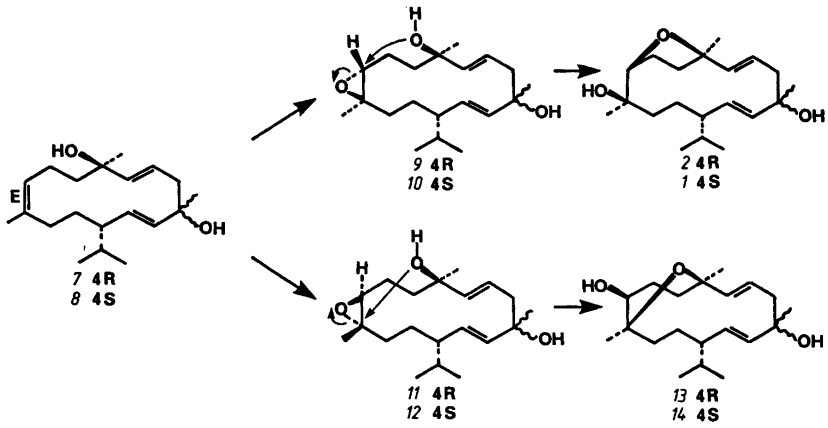
It has been proposed that the 8,11 and 8,12 ether-bridged thunberganoids are formed in tobacco as outlined in Scheme 1.[1] The 4*R*,8*R*- and 4*S*,8*R*-diols *7* and *8* are initially converted to the intermediate 11,12-epoxides *9*–*12*, which due to anchimeric assistance of the 8-hydroxyl group readily undergo an S_N2 type of opening of the 11,12-epoxy ring. Thus, (1*S*,2*E*,4*R*,6*E*,8*R*,11*S*,12*R*)-8,11-epoxy-2,6-thunbergadiene-4,12-diol (*2*) and the corresponding 4*S*-epimer *1* are formed from the 11*R*,12*R*-epoxides (*9*, *10*), whereas (1*S*,2*E*,4*R*,6*E*,8*R*,11*S*,12*R*)-8,12-epoxy-2,6-thunbergadiene-4,11-diol (*13*) and the 4*S*-epimer (*14*) are generated from the 11*S*,12*S*-epoxides (*11*, *12*). Support for this pathway is provided by the observation that peracid oxidation of the 4*S*,6*R*-diol (*15*) yields the corresponding 11,12-epoxide, which on mild acid treatment rearranges to (1*S*,2*E*,4*S*,6*E*,8*R*,11*S*,12*E*)-8,11-epoxy-2,6,12-thunbergatriene-4-ol (*16*) in quantitative yield.[4] Moreover, the isolation of the two (1*S*,2*E*,6*E*,8*R*,11*S*,12*R*)-8,11-epoxy-2,6-thunbergadiene-4,12-diols *1* and *2* and (1*S*,2*E*,4*S*,6*E*,8*R*,11*S*,12*R*)-8,12-epoxy-2,6-thunbergadiene-4,11-ol (*14*)[7] from tobacco strengthens the validity of the pathway proposed.

EXPERIMENTAL

For instrumental details: see Ref. 9.

Isolation. (1*S*,2*E*,4*S*,6*E*,8*R*,11*S*,12*R*)-8,11-Epoxy-2,6-thunbergadiene-4,12-diol (*1*, 5 mg) was isolated from a volatile neutral fraction (B8)[10] of an extract obtained from 295 kg of sun-cured Greek tobacco by repeated liquid chromatography using silica gel in the first purification step and subsequently columns packed with Bondapak C_{18}/Porasil, μBondapak C_{18} and μPorasil (Waters). *1* crystallized on standing, m.p. 105–106 °C, $[\alpha]_D$ +13.8° (*c* 0.42, $CHCl_3$). (Found: $M^{+\cdot}$ 322.2514. Calc. for $C_{20}H_{34}O_3$: 322.2508.) IR ($CHCl_3$) bands at 3500 (m), 1385 (m) and 1375 (m) cm^{-1}; ^1H NMR: δ 0.84 (3 H, d, J = 6 Hz), 0.88 (3 H, d, J = 6 Hz), 1.02 (3 H, s), 1.30 (3 H, s), 1.32 (3 H, s), 3.95 (1 H, m), 5.17 (1 H, dd, J = 8.4 and 15.4 Hz) and 5.37 (1 H, d, J = 15.4 Hz) (AB part of an ABX system), 5.44 (1 H, d, J = 15.9 Hz) and 5.58 (1 H, dt, J = 6.8 and 15.9 Hz) (AB part of an ABX_2 system); MS [*m/e* (%, composition)]: 322 (M, 1, $C_{20}H_{34}O_3$), 304 (9, $C_{20}H_{32}O_2$), 286 (2, $C_{20}H_{30}O$), 261 (7, $C_{17}H_{25}O_3$), 243 (5, $C_{18}H_{27}$), 227 (13), 206 (8, $C_{14}H_{22}O$), 177 (13), 159 (10), 135 (13), 121 (30), 109 (24), 95 (28), 81 (32), 71 (38) and 43 (100).

(1*S*,2*E*,4*R*,6*E*,8*R*,11*S*,12*R*)-8,11-Epoxy-2,6-thunbergadiene-4,12-diol (*2*, 17 mg) was isolated from a medium-volatile neutral fraction of the extract obtained from 295 kg of Greek tobacco employing liquid chromatography on silica gel and $AgNO_3$-impregnated silica gel. *2* was an oil and had $[\alpha]_D$ +2.0° (*c* 1.1, $CHCl_3$). (Found: $[M-18]^{+\cdot}$ 304.2404. Calc. for $C_{20}H_{32}O_2$: 304.2402); IR (neat) bands at 3430 (m), 1385 (m) and 1375 (m) cm^{-1}; ^1H NMR: δ 0.85 (3 H, d, J = 6 Hz), 0.89 (3 H, d, J = 6 Hz), 0.99 (3 H, s), 1.31 (3 H, s), 1.35 (3 H, s), 3.97 (1 H, m), 5.11 (1 H, dd, J = 8.7 and 15.6 Hz) and 5.40



Scheme 1. Probable biogeneses of the 8,11-epoxy-bridged tobacco diols *1* and *2* and the 8,12-epoxy-bridged tobacco diol *14*.

(1 H, d, $J = 15.6$ Hz), (AB part of an ABX system), 5.32 (1 H, dt, $J = 6.5$ and 15.6 (Hz) and 5.47 (1 H, d, $J = 15.6$ Hz) (AB part of an ABX_2 system); MS [*m/e* (%)]: 322 (M, 0.3), 304 (14), 286 (2), 261 (8), 243 (4), 227 (17), 206 (15), 177 (19), 159 (17), 139 (20), 121 (36), 109 (32), 95 (34), 81 (38), 71 (54) and 43 (100).

Preparation of the (1S,2E,4S,6E,8R,11S)-8,11-epoxy-2,6-thunbergadiene-4,12-diols epimeric at C-12 (1 and 3). A solution of 27 mg of (1*S*,-2*E*,4*S*,6*E*,8*R*,11*S*)-8, 11-epoxy-2,6,12(20)-thunbergatrien-4-ol (*4*) and 18 mg of *m*-chloroperbenzoic acid in 5 ml of dichloromethane was kept at −60 °C for 5 h, at −20 °C for 18 h and 4 °C for 5 h. The reaction mixture was diluted with water and extracted with ether. The ether extract was washed with aqueous $NaHCO_3$ and evaporated. Chromatography over silica gel yielded starting material (6 mg) and the two epimeric 12,20-epoxides *5* and *6* (7 and 8 mg). The least polar epoxide (*5*) had ^{1}H NMR: δ 0.84 (3 H, d, $J = 6$ Hz), 0.86 (3 H, d, $J = 6$ Hz), 1.32 (3 H, s), 1.34 (3 H, s), 2.68 (2 H, s), 3.46 (1 H, m), 4.9−5.8 (4 H, overlapping signals); MS [*m/e* (%)]: 320 (M, 4), 302 (2), 284 (1), 259 (2), 241 (2), 225 (3), 207 (8), 189 (5), 177 (5), 165 (8), 137 (31), 109 (33), 95 (40), 94 (38), 81 (37), 79 (39), 71 (38), 55 (38) and 43 (100). The more polar epoxide (*6*) had ^{1}H NMR: δ 0.83 (3 H, d, $J = 6$ Hz), 0.85 (3 H, d, $J = 6$ Hz), 1.33 (6 H, s), 2.48 (1 H, d, $J = 4.5$ Hz), 2.80 (1 H, d, $J = 4.5$ Hz), 3.48 (1 H, m), 4.9−5.9 (4 H, overlapping signals); MS [*m/e* (%)]: 320 (M, 5), 302 (2), 284 (1), 259 (3), 241 (3), 225 (4), 207 (8), 177 (7), 165 (8), 137 (29), 122 (15), 109 (29), 95 (37), 94 (43), 81 (32), 79 (37), 71 (33), 55 (33) and 43 (100).

A solution of epoxide *5* in ether was reacted with LAH at ambient temperature for 30 min. The reaction mixture was worked up in the usual manner and purified by chromatography over silica gel to give (1*S*,2*E*,4*S*,6*E*,8*R*,11*S*,-12*R*)-8,11-epoxy-2,6-thunbergadiene-4,12-diol (*3*) which had ^{1}H NMR: δ 0.85 (3 *H*, d, $J =$ 6 Hz), 0.89 (3 H, d, $J = 6$ Hz), 1.10 (3 H, s), 1.27 (3 H, s), 1.32 (3 H, s), 3.86 (1 H, t, $J =$ 6 Hz), 5.1−6.0 (4 H, overlapping signals); MS [*m/e* (%)]: 322 (M, 1), 304 (13), 286 (2), 261 (8), 243 (3), 227 (6), 206 (9), 177 (17), 159 (15) 135 (17), 121 (24), 109 (25), 95 (27), 81 (30), 71 (41), 55 (24) and 43 (100).

Reduction of epoxide *6* using LAH furnished (1*S*,2*E*,4*S*,6*E*,8*R*,11*S*,12*R*)-8,11-epoxy-2,6-thunbergadiene-4,12-diol, which was identical in all respects ($[\alpha]_D$, NMR, IR, MS) to one of the two new tobacco isolates (*1*).

Assignments of the ^{13}C NMR spectra of compounds 1−4 and 16. The assignment of the ^{13}C NMR spectrum of (1*S*,2*E*,4*S*,6*E*,8*R*,11*S*)-8,11-epoxy-2,6,12-thunbergatrien-4-ol (*16*) was based on LIS measurements using $Yb(fod)_3$ as the shift reagent. The relative shifts were: C-1 16; C-2 34; C-3 46; C-4 100; C-5 48; C-6 30; C-7 21; C-8 16; C-9 6; C-10 11; C-11 14; C-12 12; C-13 16; C-14 11; C-15 8; C-16 5; C-17 5; C-18 58; C-19 9; C-20 5. The measurements were made within the linear LIS range (shift reagent/substrate ratio 0−0.5) and were normalized by arbitrarily assigning the value 100 to the carbon signal exhibiting the largest shift.

A spectral comparison of *16* with *1−4* in conjunction with results from single frequency off-resonance (SFOR) decoupling and simple chemical shift considerations then solved the assignments for the last four compounds. The differentiation of the C-18 and C-20 signals for diol *2*, which was important for the determination of the chirality at C-12, was accomplished by selective proton decoupling. Thus, irradiation at the frequency of the methyl singlet at δ 0.99 (H-20) in the ^{1}H NMR spectrum selectively decoupled the carbon signal at δ 21.8, which was identified as the

C-20 signal, whereas the carbon signal at δ 24.8 which was left unaffected, was ascribed to C-18.

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