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Tobacco Chemistry. 23. Structures and Syntheses of Four New Norisoprenoid Furans from Greek *Nicotiana tabacum* L.

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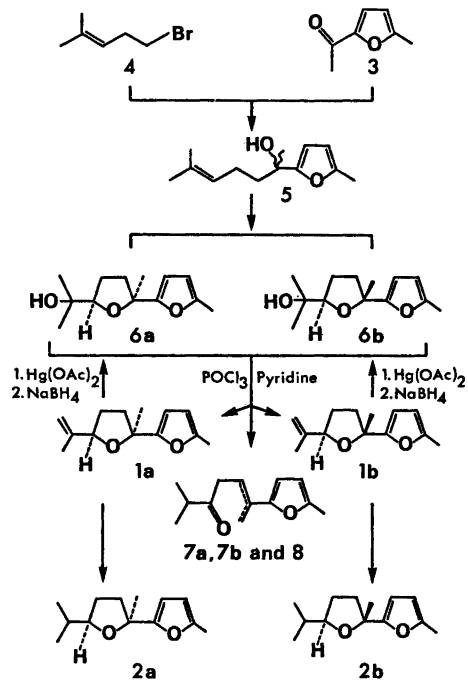
The structures of *cis* and *trans* (±)-2-methyl-5-(2-methyl-5-isopropenyltetrahydro-2-furyl)-furan, *1a* and *1b*, and their dihydro derivatives, (±)-2-methyl-5-(2-methyl-5-isopropyltetrahydro-2-furyl)furan, *2a* and *2b*, isolated from Greek tobacco were elucidated from spectral data, and subsequently confirmed by total syntheses. The *cis-trans* assignments were based upon the observation of an $Eu(DPM)_3$ induced upfield shift of the furan methyl signal in the NMR-spectrum of the *cis*-isomer of the synthetic intermediate (±)-2-[5-methyl-5-(5-methyl-2-furyl)tetrahydro-2-furyl]-2-propanol, *6a*.

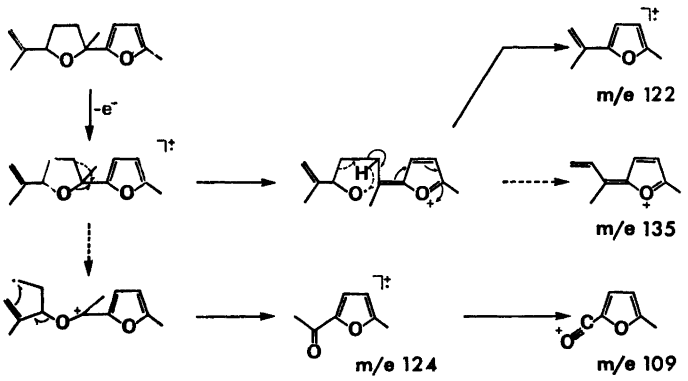
Recent research into tobacco flavour has suggested that a large number of the tobacco constituents are degradation products of terpenoid compounds.[1-3] The present communication describes the structural elucidation and syntheses of further new tobacco constituents possessing carbon skeletons derivable from those of aliphatic terpenoids.

The mass spectrum of the first isolate (from fraction C9) [4] displayed a molecular ion at *m/e* 206 corresponding to the elemental composition $C_{13}H_{18}O_2$ or $C_{14}H_{22}O$. The former alternative was favoured since signals in the NMR spectrum indicated the presence of two oxygen atoms incorporated in a furan ring and a cyclic ether. A 2-methylfur-5-yl moiety was apparent from NMR signals at δ 5.84 (1 H, doublet of quartets, J 1.0 and 3.0 Hz), δ 6.06 (1 H, doublet of quartets, J 0.4 and 3.0 Hz) and δ 2.24 (3 H, doublet of doublets, J 0.4 and 1.0 Hz).[5] The long-range spin-spin couplings between the methyl group and the furyl protons were established by spin decoupling experiments. Absence of further couplings to the proton in position 4 suggested that a fully substituted



Scheme 1.

carbon atom was attached to position 5 of the methylfuryl moiety. The second oxygen atom represented part of a cyclic ether grouping in which the two oxygenated carbon atoms carried a methyl group (δ 1.57, singlet) and an allylic proton (δ 4.45, triplet with further splittings) respectively. Double resonance experiments demonstrated that two olefinic protons (δ 4.78, 5.02) and a vinylic methyl group (δ 1.72) were weakly, mutually coupled (J *ca.* 1 Hz) and could



Scheme 2.

be ascribed to an isopropenyl group, $CH_2=C-(CH_3)-$. The remaining atoms, two methylene groups, were responsible for multiplets in the δ 1.2 – 1.8 region and were readily accomodated in the tetrahydrofuran ring of the postulated structure that could be advanced: 2-methyl-5-(2-methyl-5-isopropenyltetrahydro-2-furyl)furan. Methyl resonances of low intensity at δ 1.55 and δ 1.68 indicated that the isolate was a mixture of diastereomers (ratio 3:7). Thus both the *cis* and the *trans* tetrahydrofuran compounds (*1a* and *1b*) were present in the tobacco.

Subsequently the isomer *1a*, free of the less polar isomer (*1b*) was isolated from a more polar fraction of the tobacco by preparative gas chromatography. Its elemental composition was confirmed by accurate mass determination.

The mass spectra of the two isomers revealed prominent ions at *m/e* 109, 122, 124 and 135 for which fragments, the genesis shown in Scheme 2 may be invoked. High resolution mass spectrometry manifested the elemental compositions of the structures suggested in Scheme 2.

The mass spectrum of the second isolate, obtained by preparative gas chromatography from the same fraction [4] as *1a* and *1b*, exhibited a molecular ion at *m/e* 208, corresponding to $C_{13}H_{20}O_2$, and was similar to the mass spectra of *1a* and *1b* (abundant ions at *m/e* 109, 122, 124, and 135) indicating a structural relationship. The 2-methylfur-5-yl moiety was apparent from IR absorption at 782 cm^{-1} and signals in the NMR spectrum [5] at δ 2.26 (3 H, broad singlet), δ 5.82 (1 H, doublet with further splittings, J 3.0 Hz) and δ 6.02 (1 H, doublet, J 3.0 Hz). The methyl substituted tetrahydrofuran ring was indicated by a three-proton singlet at δ 1.54 and a one-proton multiplet at δ *ca.* 3.74. The chemical shift and multiplicity of the latter signal suggested that the proton on the oxygenated carbon was non-allylic, and that this isolate was also a diastereomeric mixture. The observed lack of clear resolution of the long-range spin couplings might be explained by small differences in chemical shifts of these protons. The diastereomeric nature (ratio 2:3) of this isolate was further supported by the presence of a seven line multiplet in the δ 0.8 – 1.0 region (6 H) which could be ascribed to two isopropyl groups. The two diastereomers could be assigned the structures *cis* and *trans* 2-methyl-5-(2-methyl-5-isopropyltetrahydro-2-furyl) furan (*2a* and *2b*).

The proposed structures of *1a*, *1b*, *2a*, and *2b* were confirmed by synthesis as outlined in Scheme 1, which also provided a means of determining their relative stereochemistry. Thus the alcohol *5*, conveniently prepared by reacting 4-methyl-3-penten-1-ylmagnesium bromide with 2-methyl-5-acetylfuran (*3*) in a Grignard reaction, was converted to a 1:1 mixture of the diastereomeric tetrahydrofuran derivatives *6a* and *6b* in one step by epoxidation followed by spontaneous cyclization.[7] Dehydration was effected by phosphorus oxychloride in pyridine to yield, after chromatography on silica, the desired pure olefins *1a* and *1b*, which exhibited spectral data and gas chromatographic behaviour (co-injection on a capillary column) indistinguishable from those of the natural mixture.

The last step also yielded three by-products evidently arising *via* rearrangement of an enol ether, namely the isomeric unsaturated ketones 2-methyl-6-(5-methyl-2-furyl)-6-hepten-3-one, (*8*), and 5*E* and 5*Z* isomers of 2-methyl-6-(5-methyl-2-furyl)-5-hepten-3-one, (*7a* and *7b*).

The pure dihydro derivatives *2a* and *2b* were prepared from *1a* and *1b*, respectively, by catalytic hydrogenation of the isopropenyl groups. Synthetic *2a* and *2b* exhibited spectral data identical to those of the natural products. The seven line multiplet in the NMR-spectrum, ascribed to the isopropyl signals, could be reconstructed by superposition of the spectra of synthetic *2a* and *2b*. Furthermore, synthetic *2a* and *2b* had different GC retention times but when coinjected separately with the natural diastereomeric mixture each, in turn, enhanced the signal for the respective natural isomer.

The relative stereochemistry of the tetrahydrofuran compounds was determined by measuring the rel. lanthanide induced chemical shifts [2,14] for the alcohols *6a* and *6b*. Attempts to separate the synthetic intermediate mixture of *6a* and *6b* were only moderately successful, even by preparative gas chromatography, and these compounds were therefore prepared by hydration [8] of the respective olefins *1a* and *1b*, which could be separated easily by liquid chromatography.

Addition of the shift reagent $Eu(DPM)_3$ to the alcohol *6* obtained from the more polar olefin *1a*, produced an upfield shift of the furan methyl signal, while for the other isomer, this signal showed the usual downfield shift. Upfield shifts are predicted for O–Eu–H angles between 54.7 and 125.3° and have been observed in a number of cases.[9] Only when the hydroxy-isopropyl group and furan ring have a *cis* relationship (*6a*) can the angle subtended by the europium atom, the hydroxyl oxygen and the furan methyl group be such as to give rise to an upfield lanthanide induced shift. Also, in a competition experiment on a 1:1 mixture, the *trans* isomer showed much stronger co-ordination to the Eu-complex.

The skeletons of these four new tobacco compounds *1a*, *1b*, *2a*, and *2b* suggest they are of terpenoid origin and pseudoionone, a known tobacco constituent,[10] could be a possible precursor. The co-occurrence of an unsaturated isoprenoid and its saturated counterpart (*e.g. 1a* and *2a*) is relatively common in tobacco isolates.[10] *1a* isolated from tobacco showed no optical activity, and it is assumed that *1a* and the related tobacco constituents described here are racemates.

EXPERIMENTAL

NMR, IR, UV, rotations, and mass spectra were recorded on Varian A60-A; HA-100D and XL-100, Digilab FTS-14, Beckmann DK-2A, Perkin-Elmer 141, and LKB 9000 (70 eV) instruments, respectively. Accurate mass determinations were carried out at the Laboratory for Mass Spectrometry, Karolinska Institutet, Stockholm. Analytical and preparative gas chromatography was performed on a Varian 1700 instrument using steel capillary columns (50 m × 0.25 mm) coated [11] with Ucon Oil HB 2000, and a 3 m × 3.2 mm glass column packed with 5 % Carbowax 20 M on Chromosorb G, respectively. The extraction of 295 kg sun-cured Greek tobacco, *Nicotiana tabacum* L., and the fractionation of the extract has been described in previous communications.[4,6] The natural compounds were isolated by preparative gas chromatography.

2-Methyl-5-(2-methyl-5-isopropenyltetrahydro-2-furyl)furan (1a+1b). Isolated as a mixture of *1a* and *1b* in ratio 3:7 (7.2 mg) from fraction C9.[4] For spectral data, see synthetic *1a* and *1b*.

(±)-cis-2-Methyl-5-(2-methyl-5-isopropenyltetrahydro-2-furyl)furan (1a): Isolated from subfraction No. 5 of fraction B2 [6] (8 mg). Spectral data are given under synthetic *1a*. Zero optical rotation was observed at λ 589, 578, 546, 436, and 365 nm.

2-Methyl-5-(2-methyl-5-isopropyltetrahydro-2-furyl)furan (2a and 2b). Isolated from fraction C9,[4] isomeric ratio 2:3. Spectral data are given under synthetic *2a* and *2b*.

Synthetic products

2-Methyl-5-acetylfuran (3) was prepared as described by Farrar and Levine.[12]

4-Methyl-3-penten-1-yl bromide (4) was obtained 95 % pure from dimethylcyclopropyl carbinol as outlined by Medina and Manjarrez [13] except for omitting the $NaHCO_3$-treatment and subsequent distillation.

(±)-6-Methyl-2-(5-methyl-2-furyl)-5-hepten-2-ol (5). 4-Methyl-3-penten-1-yl bromide (*4*, 2.6 g) in anhydrous ether (10 ml) was added dropwise to a suspension of Mg (340 mg) and ether (40 ml). Stirring was prolonged until the Mg was dissolved and the ketone (*3*, 600 mg) in ether (20 ml) was added dropwise to the cooled (0 °C) solution of the Grignard reagent. The reaction mixture was stirred for 1 h after the addition of the ketone and the temperature maintained at 0 °C. Crushed ice was added and the mixture stirred for 10 min, followed by

extraction with ether. Removal of the solvent and subsequent chromatography on silica gel furnished the furan derivative (*5*, 580 mg, 57 %) as a colourless oil. MS: *m/e* 208 (M^+, 11), 125 (100), 147 (46), 43 (33), 122 (31), 126 (18), 190 (15), 69 (15), 41 (15); $\nu_{max}^{(film)}$ 3400 (broad), 2978 (s), 2926 (s), 2860 (m), 1450 (m), 1385 (m), 1378 (m), 1221 (m), 1117 (m), 1100 (m), 1022 (s), 944 (m), 786 (s); δ ($CDCl_3$): 1.47 (3 H, s), 1.55 (3 H, m), 1.67 (3 H, m), 1.82 (2 H, m), 2.23 (3 H, d, *J* 0.8 Hz), 2.9 (OH), 5.09 (1 H, m), 5.83 (1 H, dq, *J ca.* 0.8 and 3.0 Hz), 6.03 (1 H, d, *J* 3.0 Hz).

cis *and* trans *(±)-2-[5-Methyl-5-(5-methyl-2-furyl)tetrahydro-2-furyl]-2-propanol* (6a + 6b). To a cooled (−5 °C) solution of the alcohol (*5*, 500 mg) in ether (50 ml) was added 3-chloroperbenzoic acid (600 mg) and the reaction mixture was kept at −5 °C overnight. The ether solution was extracted with diluted NaOH, washed with water, concentrated, and chromatographed on silica gel furnishing the tetrahydrofuran derivative as a colourless oil (216 mg, 40 %). The two diastereomers being present in equal amounts could only be separated by capillary GC.

cis *Isomer (6a)*. A solution of $Hg(OAc)_2.H_2O$ (171 mg) in water (0.9 ml) was diluted with tetrahydrofuran (0.9 ml) and the pure olefin *1a* (*vide infra*, the more polar of the isomers, 90 mg) added to the yellow suspension. The solution was stirred for 55 min before adding 2 M NaOH (1.5 ml) and $NaBH_4$ (15 mg). The reaction mixture was diluted with ether, washed with brine and dried (Na_2SO_4). The pale yellow residue after evaporation was chromatographed on silica (25 % ether in pentane) to yield *6a*, (39 mg). MS: *m/e* 224 (M^+, 9), 122 (100), 165 (53), 123 (43), 43 (42), 109 (21), 59 (16), 147 (13), 137 (12). IR: ν_{max}(film): 3560 (m), 3460 (broad), 3110 (w), 2980 (s), 1385 (m), 1375 (m), 1224 (m), 1092 (s), 1086 (s), 1052 (m), 1024 (s), 784 (s). NMR: The *τ* values given refer to relative induced shifts,[14] on addition of $Eu(DPM)_3$, δ ($CDCl_3$): 1.11 (3 H, s, *τ* 1.0), 1.23 (3 H, s, *τ* 0.98), 1.55 (3 H, s, *τ* 0.21), 1.7−2.3 (4 H, m), 2.25 (3 H, broad s, *τ* −0.015), 3.90 (1 H, m, *τ* 0.88), 5.85 (1 H, dq, *J* 3.0 and 1.0 Hz, *τ* 0.009), 6.04 (1 H, d, *J* 3.0 Hz, *τ* 0.13).

trans *Isomer (6b)*. It was prepared as described for the *cis* isomer but from *1b* (30 mg) to yield 11 mg. MS: *m/e* 224 (M^+, 5), 122 (100), 43 (34), 123 (28), 165 (27), 109 (16), 59 (14), 135 (9), 127 (9). IR: ν_{max}(film): 3470 (broad), 3110 (w), 2980 (s), 1386 (m), 1375 (m), 1224 (m), 1118 (s), 1056 (m), 1052 (m), 1026 (s), 1022 (s), 785 (s). NMR: For notations, see *cis* isomer. δ ($CDCl_3$): 1.15 (3 H, s, *τ* 1.0), 1.23 (3 H, s, *τ* 0.97). 1.55 (3 H, s, *τ* 0.17), 1.7−2.3 (4 H, m), 2.26 (3 H, broad s, *τ* 0.048), 3.89 (1 H, t, *J* 7.0 Hz, *τ* 0.93), 5.85 (1 H, dq, *J* 3.0 and 1.0 Hz, *τ* 0.048), 6.05 (1 H, d, *J* 3.0 Hz, *τ* 0.12).

(±)-2-Methyl-5-(2-methyl-5-isopropenyltetrahydro-2-furyl)furan (1a and 1b). To a cooled (−10 °C) solution of the diastereomeric alcohols *6a* and *6b* (500 mg) in dry pyridine (50 ml) was added $POCl_3$ (1.5 ml) dissolved in pyridine (5 ml). The mixture was kept at −10 °C for 24 h, diluted with water and extracted with ether. The extract was washed with diluted H_2SO_4, water, $NaHCO_3$, water, concentrated and chromatographed on silica gel. The two diastereomers *1a* and *1b* were separated and collected in fractions 2 and 1, respectively. Three slightly more polar products (double-spot on TLC) were found in fraction 3 (160 mg). ν_{max}(film): 1714 cm^{-1}; NMR of fraction 3 revealed the presence of the following three compounds (ratio *ca.* 5:1:4) :2-methyl-6-(5-methyl-2-furyl-5*E*-hepten-3-one, (*7a*), δ 1.91, (3 H, m), δ 3.34 (2 H, d, *J* 7 Hz); irradiation at δ 6.18, and δ 1.91 respectively simplified the multiplet at δ 1.91, and increased (6 %) the intensity of the doublet at δ 3.34, 2-methyl-6-(5-methyl-2-furyl)-5*Z*-hepten-3-one, (*7b*, δ 2.02 (*ca.* 3 H, m), δ 3.66 (*ca.* 2 H, d, *J* 7 Hz), and 2-methyl-6-(5-methyl-2-furyl)-6-hepten-3-one (*8*), δ 4.89 (1 H, m), δ 5.45 (1 H, m). Signals also occurred at δ 1.12 (6 H, dd), δ 2.30 (3 H, m), δ *ca.* 2.66 (*ca.* 4 H, m), δ 5.95 (1 H, m), δ *ca.* 6.18 (*ca.* 2 H, m). Less of the desired olefins and more of these side-products were produced when higher reaction temperatures were employed.

trans *Isomer (1b)* (70 mg, yield: 31 %, based on the weight of one of the diastereomers of *6*): MS: *m/e* 206 (M^+, 6), 109 (100), 43 (55), 124 (48), 67 (37), 122 (27), 121 (21), 125 (20), 41 (16), 82 (14); ν_{max}(film): 1373 (m), 1301 (w), 1262 (m), 1221 (m), 1181 (w), 1149 (w), 1100 (s), 1044 (m), 1020 (s), 958 (w), 943 (w), 900 (s), 873 (w,) 784 (s); δ ($CDCl_3$): 1.58 (3 H, s), 1.73 (3 H, m), 2.24 (3 H, dd, *J* 1.0 and 0.4 Hz), 4.45. (1 H, t, *J ca.* 6.5 Hz), 4.79 (1 H, broad s), 5.02 (1 H, broad s), 5.83 (1 H, dq, *J* 1.0 and 3.0 Hz), 6.05 (1 H, d, *J* 3.0 and 0.4 Hz). Irradiation at δ 1.73 simplified the peaks at δ 4.79 and 5.02, while irradiation at δ 2.24 simplified the signals at δ 5.83 and 6.05 to doublets. No separation from the natural isomer could be observed when co-injected with fraction B1 on a capillary GC column.

cis *Isomer (1a)* (75 mg, yield 33 %). MS: *m/e* 206 (M^+, 17), 109 (100), 43 (78), 67 (30), 122 (26), 148 (25), 135 (25), 41 (23), 124 (23), 121 (20).

Accurate mass determinations (measured on natural *1a*)

Composition:	$C_{13}H_{18}O_2$	$C_9H_{11}O$	$C_7H_8O_2$	$C_8H_{12}O$
found =	206.1311	135.0807	124.0524	124.0888
calc. =	206.1307	135.0810	124.0524	124.0888

Composition:	$C_8H_{10}O$	$C_6H_5O_2$	C_7H_9O	C_8H_{13}
found =	122.0739	109.0286	109.0657	109.1022
calc. =	122.0732	109.0290	109.0653	109.1017

The tree ions at *m/e* 109 are given in the order of decreasing abundance. ν_{max}(film): 1373 (m), 1309 (w), 1289 (w), 1269 (w), 1222 (m), 1206 (w),

1181 (w), 1153 (m), 1100 (s), 1022 (s), 982 (w), 960 (w), 946 (w), 928 (w), 901 (s), 870 (w), 848 (w), 785 (s); δ ($CDCl_3$): 1.56 (3 H, s), 1.69 (3 H, m), 2.23 (3 H, dd, J 0.4 and 1.0 Hz), 4.46 (1 H, m), 4.78 (1 H, broad s), 5.0 (1 H, broad s), 5.81 (1 H, dq, J 1.0 and 3.0 Hz), 6.05 (1 H, dq, J 0.4 and 3.0 Hz).

The synthetic product was indistinguishable from the natural compound isolated from fraction B2 when coinjected on a capillary GC column.

trans (±)-*2-Methyl-5-(2-methyl-5-isopropyltetrahydro-2-furyl)furan (2b). 1b* (22 mg) in ethanol (2 ml) was hydrogenated at room temperature and atmospheric pressure using platinum oxide (*ca.* 5 mg) as catalyst. The hydrogen uptake was completed in 10 min and the reaction mixture was diluted with water and extracted with pentane. Removal of the solvent furnished the dihydro derivative (19 mg) essentially pure. MS: *m/e* 208 (M^+, 5), 43 (100), 41 (40), 109 (32), 69 (19), 55 (19), 193 (16), 165 (15), 123 (11), 122 (10), 121 (8), 125 (8), 124 (6); ν_{max}(film): 1388 (m), 1371 (m), 1278 (w), 1222 (m), 1178 (w), 1105 (m), 1047 (s), 1022 (s), 958 (w), 944 (w), 902 (w) 869 (w), 785 (s); δ ($CDCl_3$): 0.88 (3 H, d, J 6.8 Hz), 0.95 (3 H, d, J 6.0 Hz), 1.53 (3 H, s), 2.24 (3 H, d, J 1.0 Hz), 3.78 (1 H, q, J *ca.* 6.5 Hz), 5.83 (1 H, dq, J 1.0 and 3.0 Hz), 6.02 (1 H, d, J 3.0 Hz).

cis(±)-*2-Methyl-5-(2-methyl-5-isopropyltetrahydro-2-furyl)furan (2a). 1a* (28 mg) was hydrogenated as described above yielding the pure dihydro derivative (27 mg). MS: *m/e* 208 (M^+, 9), 43 (100), 109 (73), 69 (40), 193 (35), 165 (32), 41 (30), 123 (28), 125 (25), 124 (20), 55 (20), 121 (15), 122 (13); ν_{max}(film): 1386 (m), 1370 (m), 1290 (w), 1279 (w), 1221 (m), 1108 (s), 1041 (m), 1025 (s), 958 (w), 945 (w), 918 (w), 901 (w), 845 (w), 785 (s); δ ($CDCl_3$): 0.84 (3 H, d, J 6.8 Hz), 0.98 (3 H, d, J 6.5 Hz), 1.51 (3 H, s), 2.21 (3 H, dd, J 0.4 and 1.0 Hz), 3.72 (1 H, q, J *ca.* 7 Hz), 5.80 (1 H, dq, J 1.0 and 3.0 Hz), 6.02 (1 H, dq, J 0.4 and 3.0 Hz). The two dihydro derivatives could only be separated on capillary GC columns and were found indistinguishable from the natural diastereomeric mixture when co-injected.

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