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Tobacco Chemistry. 28. Structure and Synthesis of Drim-8-en-7-one, a New Tobacco Constituent

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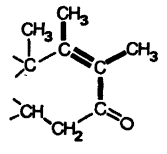
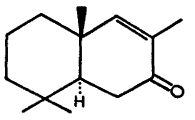
A new sesquiterpene ketone of the drimane series was isolated from Greek *Nicotiana tabacum* L. and shown to be drim-8-en-7-one** (*10*). This structure was subsequently confirmed synthetically using drimenol (*3*) as starting material.

Research on tobacco flavour has revealed that the material released as head-space volatiles or produced during the smoking-process comprises numerous constituents [1–4] of which a large number has been characterized as degradation products of terpenoids of either the carotenoid or the thunbergane-type.[5–10] Tobacco is also known to produce diterpenoids of the labdane-class [11–15] and earlier this year we reported on the structures and syntheses of five new natural products [16–18] which, together with norambreinolide [19] and six other very recently published tobacco constituents,[20] can be viewed as either being genuine sesquiterpenoids of the drimane group, or products derived from labdanes. We now wish to discuss the identification and confirmative synthesis of another bicyclic, terpenoid tobacco constituent which can be allotted to the drimane/labdane-derived category.

The compound was isolated in minute quantities from a medium-polar, neutral fraction (B4) [10] previously obtained from an ether-extract of sun-cured Greek *Nicotiana tabacum* L. and the structure gleaned exclusively from spectral properties. The presence of a conjugated, disubstituted, endocyclic enone system was indicated from UV [21] and IR absorption (248.5 nm, 1612 and 1661 cm^{-1}). Two mutually spin-spin coupled three-proton resonances [22] (homoallylic coupling [23] *ca.* 1 Hz) at δ 1.74 (α-CH_3) and δ 1.84 (β-CH_3) verified this and showed the two substituents to be methyls. With no evidence in the NMR spectrum of oxygen substituents or unsaturations apart from the enone moiety, and the elemental composition $C_{15}H_{24}O$ for the ion at highest mass, a bicyclic, conjugated ketone was implied which is in accord with the polarity of the fraction under investigation. The appearance of a two-proton multiplet in the δ 2.17 – 2.66 region as the AB-part of an ABC-system revealed that a methylene group, in turn linked to a methine group, was attached to the carbonyl group. These data and the presence of three methyl singlets at δ 0.88, 0.92 and 1.09, the last one assigned to a methyl group on a vinylic, quaternary carbon atom, implied the partial structure *1*. Since this partial structure contains the tail-end of three head-to-tail-linked isoprene units, implied by the C_{15}-structure comprising five methyl groups, the complete structure, *10*, disregarding stereochemistry, may be advanced for the new compound.



1



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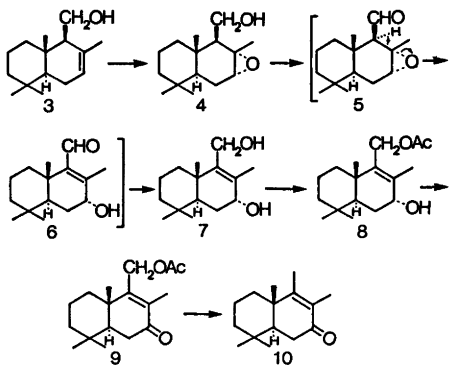
This was verified by comparison of its spectral data with those of (4a*R*,8a*S*)-4a,5,6,7,8,8a-hexahydro-3,4a,8,8-tetramethylnaphthalen-2(1H)-one (*2*, 11-nordrim-8-en-7-one) which recently

** Nomenclature and stereochemistry as defined in Ref. 25.

has been identified by us as a constituent of the same tobacco.[16] Thus the NMR and mass spectra of the two compounds were quite similar except for features expected on the basis of structural differences, *i.e.* the new tobacco isolate exhibited the molecular and base peaks fourteen mass units above those of *2*, and displayed an additional vinylic methyl signal (δ 1.84), but lacked the olefinic resonance of the 11-nor derivative *2*.

The assigned structure, drim-8-en-7-one (*10*), was unequivocally established by synthesis using drimenol [24,25] as starting material, see Scheme 1. 7α,8-Epoxydriman-11-ol (*4*),[25] prepared by epoxidation of drimenyl acetate, was converted in good yield to drim-8-en-7α-11-diol (*7*) in three steps. These were performed *in situ* and involved oxidation to the epoxyaldehyde *5* followed by base-catalyzed isomerization to the conjugated aldehyde *6*, and hydride-reduction of this aldehyde *7*. On attempted characterization the intermediates *5* and *6* proved unstable. Acetylation of the diol *7* at reduced temperature furnished 11-acetoxydrim-8-en-7α-ol (*8*) as the major product which on oxidation with Jones' reagent [26] yielded the keto-ester *9*. Hydrogenolysis of the conjugated keto-ester *9* applying zinc in acetic acid [27] gave drim-8-en-7-one (*10*) in excellent yield and this product was found identical to the tobacco constituent. Since the absolute configuration of drimenol (*3*) has previously been established [25] by correlation to oleanolic [28] and abietic acid [29] and, since synthetic and natural *10* exhibited rotatory powers of similar magnitude and the same sign, it follows that the absolute configuration of the natural ketone *10* at C-5 and C-10 are as shown in formula *10* (both centres have *S*-configuration).



Scheme 1.

The final product and the intermediates *3* – *9* are structurally related to a large number of oxygenated *trans*-decalins which exhibit a typical ambra odour.[30,31] However, the present *trans*-decalins are devoid of any significant smell thus implying that they do not meet the spacial requirements of the receptor sites of the human olfactory system.

We have previously isolated five structurally related compounds, (4a*R*,8a*S*)-4a,5,6,7,8,8a-hexahydro-3,4a,8,8-tetramethylnaphthalen-2(1*H*)-one (*2*),[16] (1'*S*,6'*R*)-4-(2',2',6'-trimethyl-6'-vinylcyclohexyl)-2-butanone (*13*),[16]* 14,15-bisnor-8-hydroxylabd-11*E*-en-13-one (*14*),[17] driman-8-ol (*15*),[18] and driman-8,11-diol (*16*),[18] from the same tobacco. A question of considerable interest is if these and the new compound (*10*), whose structures have been confirmed by syntheses from drimenol (*3*), all are degradation products of labdane diterpenoids or if only one (*14*) is of this origin and the others are true drimane sesquiterpenoids (*10*, *15*, *16*) and derivatives thereof (*2*, *13*). While the number and amounts of labdane diterpenoids predominate over those of the C_{14} and C_{15} compounds, as might be expected if they were precursors, no conclusion can be drawn from the steric relationships and valid arguments in favour of this alternative has to await tracer-studies and/or degradation studies such as photooxygenations of labdane diterpenoids.

EXPERIMENTAL

NMR, IR, UV, rotations and mass spectra were recorded on Varian XL-100, Digilab FTS-14, Perkin-Elmer 257, Beckmann DK-2A, Perkin-Elmer 141, and LKB 9000 instruments, respectively. Melting points were obtained using a Leitz Wetzlar instrument and are uncorrected. 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

* In the original publication (Hlubucek *et al. Acta Chem. Scand. B 28* (1974) 18) the configuration and formula of this compound are correct but the Cahn, Ingold, Prelog-convention was incorrectly appiied with respect to the designation of the configuration at C(6').

capillary columns (50 m × 0.25 mm) coated with Ucon Oil HB 2000,[32] 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., grown in Serres 1968, and the fractionation of the extract have been described in a previous communication.[10] The present compound was isolated subfraction B4,[10] the further components of which will be published later.[33]

Drim-8-en-7-one (*10*) was isolated (4 mg) from subfraction No. 2 of B4[10] by liquid chromatography on alumina followed by preparative gas chromatography. For spectral data other than those listed here, *cf.* synthetic drim-8-en-7-one (*10*). $[\alpha]^{20}$ +58.7° (589 nm), +60.0° (578), +70.7° (546), +166.7° (436), +736.7° (365) (*c* 0.2; $CHCl_3$); λ_{max} ($CHCl_3$): 248.5 nm (ε 7060); accurate mass measurements: C_6H_9O, found 97.0652, calc. 97.0653; $C_{15}H_{24}O$, found 220.1829, calc. 220.1827.

Synthetic products

7α,8-Epoxydriman-11-ol (*4*). Drimenol (*3*, 196 mg), $[\alpha]^{20}$ −22° (589 nm), −22° (578), −25.2° (546), −46° (436), −82° (365) (*c* 0.5; benzene), lit.:[24] $[\alpha]_D^{25}$ −19.1° (benzene), was dissolved in dry pyridine (10 ml) and acetic anhydride (3 ml) and kept at room temperature for 24 h. The acetate (230 mg) isolated in the usual manner, was dissolved in CH_2Cl_2 (35 ml) and cooled in a dry-ice/acetone bath. A cooled solution of *m*-chloroperbenzoic acid (320 mg) in CH_2Cl_2 was added dropwise and the reaction mixture kept at −50 °C for 48 h. Water was added to the mixture which was extracted with CH_2Cl_2. The extract was washed with $NaHCO_3$, brine, and evaporated to dryness. The acetate was hydrolyzed with 5 % KOH/CH_3OH (10 ml) at room temperature within 1 h. Dilution with water and extraction with ether furnished after removal of the solvent, a crystalline residue which was recrystallized from pentane/ether. The crystals (154 mg) consisted solely of the 7α,8-epoxide, while the mother liquor (75 mg) contained a mixture of the 7α,8-epoxide and the 7β,8β-epoxide. The 7α,8-epoxide possessed the following physical properties: MS: 238 (M^+, 1.1), 109 (100), 123 (73), 69 (71), 41 (67), 124 (53), 95 (49), 81 (47), 55 (47), 177 (47), 43 (42), 138 (36), 191 (36); $\delta(CDCl_3)$: 0.79 (3 H, s), 0.87 (6 H, s), 1.49 (3 H, s), 3.02 (1 H, m, W_H = 5 Hz), 3.66 (1 H, q, *J* 9.5 and 11.5 Hz), 3.98 (1 H, q, *J* 3.5 and 11.5 Hz); ν_{max} (KBr): 3475 (s), 2966 (s), 2931 (s), 2920 (s), 1441 (s), 1392 (s), 1378 (m), 1368 (m), 1240 (m), 1048 (s), 1038 (m), 991 (m), 983 (m), 949 (s), 925 (m), 851 (s), 760 (s), 700 (m); $[\alpha]^{20}$ +14° (589 nm), +17° (578), +18° (546), +29° (436), +38° (365) (*c* 0.2; $CHCl_3$), lit.:[25] $[\alpha]_D$ +20° (*c* 1.56; $CHCl_3$); m.p. 98–99 °C, lit.:[25] 96–97 °C. The epoxyalcohol *4* could also be prepared directly from drimenol by epoxidation analogous to the procedure of Appel *et al.*[25] but the yields of the 7α,8-epoxide appeared to be lower.

Drim-8-en-7α,11-diol (*7*). Brown's [34] reagent (1 ml) was added to a solution of 7α,8-epoxydriman-11-ol (*4*, 100 mg) in ether (30 ml) and the mixture stirred at room temperature for 20 min. When the conversion to the aldehyde, 7α,8-epoxydriman-11-al (*5*), was complete (TLC), excess CrO_3 was destroyed by the addition of methanol (1.5 ml) and the stirring continued for 10 min. Methanolic potassium hydroxide (2 ml, 5 %) was added to the mixture and the isomerization to the conjugated aldehyde, 7α-hydroxydrim-8-en-11-al (*6*), was followed by TLC. The isomerization was complete after 30 min at room temperature as shown by the appearance of a single, UV-visible, more polar spot. Excess $NaBH_4$ (200 mg) was added and the mixture stirred for another 10 min. When the UV-visible TLC-spot had dissappeared, water (20 ml) was added and the mixture extracted four times with CH_2Cl_2. The extract was washed with brine, dried over Na_2SO_4, and the solvent distilled. The white, solid residue (80 mg) was recrystallized from ether/CH_3OH. MS: M^+ at *m/e* 238 not visible, 207 (100), 109 (91), 119 (91), 123 (65), 69 (52), 41 (52), 43 (48), 55 (44), 220 (39), 95 (39); $\delta(CD_3OD)$: 0.88 (3 H, s), 0.93 (3 H, s), 0.97 (3 H, s), 1.83 (3 H, s), 3.92 (1 H, t with further splittings), 4.07 (1 H, d, *J* 12 Hz), 4.18 (1 H, d, *J* 12 Hz), AB-system; ν_{max} (KBr): 3250 (s), 2945 (s), 1460 (m), 1390 (m), 1378 (m), 1214 (m), 1060 (s), 1026 (m), 1019 (m), 991 (s), 976 (m), 880 (m); $[\alpha]^{20}$ +113° (589 nm), +118° (578), +136° (546), +246° (436), +408° (365) (*c* 0.1; methanol); m.p. 196–197 °C. The epoxyaldehyde *5* which also could be prepared from the epoxyalcohol *4* employing Sarrett's reagent (CrO_3-pyridine complex),[35] was attempted isolated and purified by liquid chromatography, but was found very unstable.

Selective acetylation of drim-8-en-7α,11-diol (*7*). The diol *7* (38 mg) dissolved in dry pyridine (2 ml) and two equivalents acetic anhydride (33 mg) was kept at 0 °C for 48 h. The reaction mixture was diluted with water and extracted four times with ether. The extract was washed with diluted H_2SO_4, $NaHCO_3$, water, and evaporated. The residue was carefully chromatographed on silica gel and the diacetate, 7α,11-diacetoxy-8-drimene (*11*, 7 mg) was eluted with 10 % ether in pentane, the monoacetates, 11-acetoxydrim-8-en-7α-ol (*8*, 23 mg) and 7α-acetoxydrim-8-en-11-ol (*12*, 9 mg) was eluted with 25 % ether in pentane, the latter monoacetate was the more polar, and unreacted diol (*7*, 9 mg) was eluted with pure ether.

7α,11-Diacetoxy-8-drimene (*11*). MS: M^+ at *m/e* 322 not visible, 262 (13, M^+ − AcOH), 220 (100), 43 (88), 119 (80), 133 (47), 187 (38), 41 (36), 205 (33), 189 (31); $\delta(CDCl_3)$: 0.84 (3 H, s), 0.86 (3 H, s), 0.96 (3 H, s), 1.66 (3 H, s), 2.06 (3 H, s), 2.08 (3 H, s), 4.10 (2 H, broad s), 5.20

(1 H, t with further splittings); ν_{max} (film): 2933 (s), 1740 (s), 1446 (m), 1375 (s), 1236 (s), 1159 (w), 1022 (s), 981 (m), 967 (m), 939 (m), 919 (w), 848 (w); $[\alpha]^{20}$ +96.3° (589 nm), +100.9° (578), +116.1° (546), +214.3° (436), +373.9° (365) (*c* 0.46; $CHCl_3$).

11-Acetoxydrim-8-en-7α-ol (8). MS: M+ at *m/e* 280 not visible, 262 (5, M+ $-H_2O$), 220 (100), 43 (69), 123 (64), 119 (44), 109 (44), 97 (43), 41 (43), 69 (40), 135 (34), 55 (34), 205 (31), 133 (31); $\delta(CDCl_3)$: 0.86 (3 H, s), 0.93 (3 H, s), 0.94 (3 H, s), 1.81 (3 H, s), 2.05 (3 H, s), 4.0 (1 H, t with further splittings), 4.50 (2 H, s); ν_{max} (film): 3300 (m), 2930 (s), 1740 (s), 1461 (m), 1387 (m), 1378 (m), 1240 (s), 1158 (w), 1138 (w), 1058 (m), 1026 (m), 1005 (m), 985 (m), 961 (m), 885 (w); $[\alpha]^{20}$ +128.6° (589 nm), +132.9° (578), +148.6° (546), +270° (436), +453.6° (365) (*c* 0.14; $CHCl_3$).

7α-Acetoxydrim-8-en-11-ol (12). MS: M+ at *m/e* 280 not visible, 220 (93, M+ −AcOH), 109 (100), 119 (58), 43 (56), 95 (44), 41 (44), 124 (40), 97 (40); $\delta(CDCl_3)$: 0.85 (3 H, s), 0.86 (3 H, s), 0.97 (3 H, s), 1.75 (3 H, s), 2.08 (3 H, s), 4.12 (1 H, d, *J* 12 Hz), 4.24 (1 H, d, *J* 12 Hz), 5.21 (1 H, t with further splittings); ν_{max}(KBr): 3440 (m, broad), 2960 (s), 2938 (s), 1732 (s), 1461 (m), 1379 (m), 1245 (s), 1211 (m), 1018 (m), 989 (m), 965 (m), 951 (m), 938 (m), 881 (m), 849 (m); $[\alpha]^{20}$ +102.5° (589 nm), +110° (578), +122.5° (546), +240° (436), +432.5° (365) (*c* 0.1; $CHCl_3$); m.p. 144–145 °C.

11-Acetoxydrim-8-en-7-one (9). To a solution of 11-acetoxydrim-8-en-7α-ol (*8*, 13 mg) in acetone (3 ml) was added a few drops of Jones' reagent [26] and the mixture stirred at ambient temperature for 30 min and the oxidation followed by TLC. The mixture was diluted with water and extracted with ether twice. The extract was washed with $NaHCO_3$, water and evaporated to yield pure (TLC) ketone *9* (10 mg, 78 %). The ketone *9* could also be prepared from the alcohol *8* in excellent yield employing Brown's two-phase system.[34] MS: 278 (M+, 17), 205 (100), 43 (89), 135 (74), 236 (42), 41 (41), 113 (38), 123 (36), 69 (36), 55 (31); $\delta(CDCl_3)$: 0.90 (3 H, s), 0.94 (3 H, s), 1.13 (3 H, s), 1.80 (3 H, s), 2.09 (3 H, s), *ca.* 2.4 (H_A, 'q', J_{AC} *ca.* 12 Hz, J_{AB} *ca.* 18 Hz), *ca.* 2.53 (H_B, 'q', J_{BC} *ca.* 6 Hz, J_{AB} *ca.* 18 Hz), 4.73 (1 H, d, *J* 12 Hz), 4.79 (1 H, d, *J* 12 Hz); ν_{max} (film): 2932 (s), 1742 (s), 1671 (s), 1622 (w), 1465 (m), 1446 (m), 1379 (s), 1321 (m), 1232 (s), 1153 (m), 1140 (m), 1029 (s), 970 (m), 919 (w), 781 (w), 758 (w); $[\alpha]^{20}$ +60.6° (589 nm), +64.5° (578), +76.4° (546), +181.2° (436), +587.9° (365) (*c* 0.3; $CHCl_3$); λ_{max} ($CHCl_3$): 245 nm (ε 10 530).

Drim-8-en-7-one (10). 11-Acetoxydrim-8-en-7-one (*9*, 10 mg) dissolved in acetic acid (2.5 ml) was stirred for 30 min at room temperature in the presence of activated Zn (400 mg).[36] The reduction [27] to *10* was monitored by TLC and when complete the mixture was poured into a saturated solution of $NaHCO_3$ and extracted with ether twice. Evaporation of the solvent left the ketone (8 mg, 100 %), essentially pure by TLC, as a colourless oil which crystallized on storage at 0 °C. MS: 220 (M+, 40), 97 (100), 135 (40), 69 (30), 41 (30), 123 (27), 55 (23), 109 (19), 137 (17); $\delta(CDCl_3)$: 0.88 (3 H, s), 0.92 (3 H, s), 1.09 (3 H, s), 1.74 (3 H, q, *J* *ca.* 1 Hz), 1.84 (3 H, q, *J* *ca.* 1 Hz), 2.17–2.66 AB-part of an ABC-system: *ca.* 2.34 (H_B, 'q', J_{BC} *ca.* 12 Hz, J_{AB} *ca.* 17 Hz), *ca.* 2.52 (H_A, 'q', J_{AC} *ca.* 6 Hz, J_{AB} *ca.* 17 Hz); ν_{max} (film): 2929 (s), 2869 (m), 2851 (m), 1661 (s), 1612 (m), 1460 (m), 1377 (m), 1324 (m), 1256 (w), 1216 (w), 1152 (w), 1140 (w), 1090 (w), 1076 (m), 1059 (w), 980 (w), 962 (w), 935 (w), 914 (w), 780 (w), 685 (w), 621 (w); $[\alpha]^{20}$ +49.6° (589 nm), +51.9° (578), +62.8° (546), +154.4° (436), +720° (365) (*c* 0.8; $CHCl_3$); λ_{max} ($CHCl_3$): 248 nm (ε 7100); m.p. 52–53 °C. The NMR, IR, and mass spectra of synthetic drim-8-en-7-one (*10*) were superimposable on those of the new tobacco isolate. Furthermore, the two compounds were indistinguishable when coinjected on a capillary GC-column.

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