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4,8,13-DUVATRIENE-1-OL-3-ONE AND 11-ISOPROPYL-4,8-DIMETHYL-3,7,12-PENTADECATRIENE-2,14-DIONE ISOMERS FROM *NICOTIANA TABACUM*

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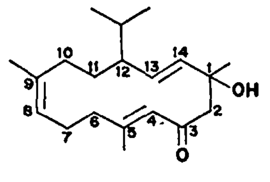
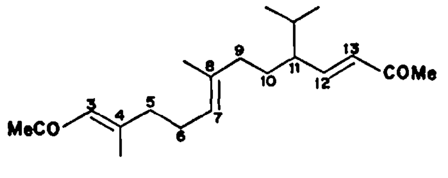
Key Word Index—*Nicotiana tabacum*; Solanaceae; dark-fired fermented tobacco; terpenoid diketones; 4,8,13-duvatriene-1-ol-3-one; 11-isopropyl-4,8-dimethyl-3,7,12-pentadecatriene-2,14-dione.

Plant. Nicotiana tabacum. Source. Grown commercially in north-western Tennessee, and smoke-cured in barns. *Uses.* Mostly for snuff manufacture. *Previous work.* None on diterpenes or dark-fired tobacco. A number of diterpenoids have been isolated, however, from other tobaccos.[1,2]

Present work. The present report describes the isolation, for the first time from a natural source, of three compounds which were produced in the tobacco leaf during a natural fermentation process. These compounds are, 4,8,13-duvatriene-1-ol-3-one (I), the diketone, 11-isopropyl-4,8-dimethyl-3,7,12-pentadecatriene-2,14-dione (II). The latter was obtained in two stereo forms, as isomers-*A* and -*B*. Compounds I and II constituted 0·08 and 0·02% respectively by weight of dry tobacco. It is conceivable that these products are formed by enzymatic action on the α- and β-4,8,13-duvatriene-1,3-diols which are known to be present in the tobacco leaf. These diols have been previously reported to be present in burley, flue-cured and Turkish tobaccos.[1]



(I)



(II)

Compound I was a yellow oil, $C_{20}H_{32}O_2$ (M^+304). UV: λ_{max}^{EtOH} 243 nm (ε 9300). IR ν_{max} (NaCl disc): 3440, 1676, 1613, 1440, 1386, 1368, 1290 1210, 978, 935 cm^{-1}. NMR (60 MHz, $CDCl_3$): τ 9·14 (*q*, 6H), 8·63 (*s*, 3H), 8·42 (*s*, 3H), 7·91 (*d*, 3H, *J* 1·4 Hz), 5·04 (*s*, 1H), 4·55 (*t*, 2H), 3·94 (*s*, 1H). The structure of I was established by the preparation of authentic α- and β-4,8,13-duvatriene-1-ol-3-ones.[1] Since a mixture of the synthetic diesastero-isomers were not separable on the GLC or the chromatographic columns tried, (I) could be an unresolvable mixture of the α- and β-forms.

Compound II consisted of isomers-*A* and -*B* in the proportion of 1–4. *Isomer* B was a yellow oil, $C_{20}H_{32}O_2$ (M^+ 304). UV λ_{max}^{EtOH} 229 nm (ε 21 800). IR ν_{max} (NaCl disc): 1688,

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[1] D. L. ROBERTS and R. L. ROWLAND, *J. Org. Chem.* **27**, 3989 (1962); **28**, 1165 (1963); **29**, 16 (1964).

[2] A. J. AASEN, B. KIMLAND, S. O. ALMQVIST and C. R. ENZELL, *Acta Chem. Scand.* **26**, 832 (1972).

1676, 1620, 1386, 1360, 1252, 1212, 1168, 983 cm^{-1}. NMR (60 MHz, $CDCl_3$): τ 9·12 (*q*, 6H), 8·41 (*s*, 3H), 7·87 (*d*, 3H *J* 1·0 Hz), 7·84 (*s*, 3H), 7·75 (*s*, 3H), 3·1–5·0 (4H). The physical data compares closely with those published for the synthetic material.[1] *Isomer*-A was a yellow oil. (Found: C, 78·52; H, 10·50. $C_{20}H_{32}O_2$ requires: C, 78·89; H, 10·59%.) UV λ_{max}^{EtOH} 229 nm (ϵ 17 700). IR ν_{max} (NaCl disc). 1686, 1672, 1615, 1384, 1356, 1252, 1168, 982 cm^{-1}. NMR (60 MHz, $CDCl_3$): τ 9·10 (*q*, 6H), 8·38 (*s*, 3H), 8·13 (*d*, 3H *J* 1·5 Hz), 7·85 (*s*, 3H), 7·75 (*s*, 3H), 3·1–5·0 (4H).

Stereochemistry of isomers-A *and* -B. The 7,8-double bonds in both isomers are assigned the *trans* configuration, that is, by applying Bates' observations to the NMR data.[3] The disubstituted 12,13-double bond is also of *trans* form.[1] The location of the peak for the methyl group at τ 7·87 in the isomer-*B* and at τ 8·13 in the isomer-*A* suggests that the 3,4-double bond is *cis* in isomer-*A* and *trans* in isomer-*B*. Analogy is drawn from chemical-shift data for *cis-trans* pairs of unsaturated esters where the deshielding of the protons of a *cis* methyl group by an alkoxy-carbonyl group is fairly constant, being of the order of 0·25 Hz.[4]

EXPERIMENTAL

Dark-fired and aged tobacco (U.S. Department of Agriculture Types 22 and 23) were wetted with H_2O to produce a 40–43% moisture content. The leaves were ground to a 6-mm size and stored at 23–25° in thin, opaque polyethylene bags. Once a week the bags were uncovered for about 5 min aeration. The progress of the fermentation was followed by GLC (OV-101) by sampling the tobacco at 8-day intervals. After 50 days the tobacco was air-dried, ground and extracted with cold hexane. The extract was chromatographed on silicic acid columns. The desired materials were found in the 10% Et_2O–C_6H_6 fractions. Compound II, which preceded I off the column, was further purified and separated into two stereo forms (*A* and *B*) on a florisil column using 50% Et_2O–C_6H_6.

Isomerization of isomers-A *and* -B. Distillation of isomer-*B* at 170° 0·2 mm Hg pressure produced about equal amounts of isomer-*B* and isomer-*A*. Similarly, the distillation of isomer-*A* produced about equal amounts of the two isomers. MS of *A* and *B* were identical.

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[3] R. B. BATES and D. M. GALE, *J. Am. Chem. Soc.* **82**, 5749 (1960).

[4] L. M. JACKMAN and R. H. WILEY, *J. Chem. Soc.* 2886 (1960).

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SIMIARENONE FROM *TREMA ORIENTALIS*[*]

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Key Word Index—*Trema orientalis*; Ulmaceae; triterpene; simiarenone.

Repeated chromatographic fractionation on alumina of the neutral fraction of the light petrol. extract of the stem-bark of *Trema orientalis* gave a crystalline ketone (0·04% based

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[*] L. OGUNKOYA, O. O. OLUBAJO and D. S. SONDHA, *Phytochem.* **11**, 2361 (1972).