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TOBACCO CHEMISTRY 5

NOR-SOLANESENE, A C_{44}-ISOPRENOID HYDROCARBON FROM TOBACCO

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In continuation of our studies of Greek tobacco (Serres 1968)[1-3], we have examined a fraction comprising unsaturated hydrocarbons of higher molecular weight. Repeated chromatography on silica gel and $AgNO_3$-impregnated silica gel furnished squalene (0.004 % of dry tobacco), previously encountered in tobacco, and a new hydrocarbon (0.0005 % of dry tobacco). The present paper provides evidence for assigning structure 1 to the latter compound, now named nor-solanesene (all-trans 2,6,10,14,18,22,26,30,34-nonamethyl-1,5,9,13,17,21,25,29,33-pentatriacontanonaene), and deals with its synthesis from solanesol (2).

The mass spectrum of nor-solanesene (Fig. 1) exhibits a fairly strong molecular peak, shown by high resolution studies to correspond to an ion of the composition $C_{44}H_{72}$ (Found:

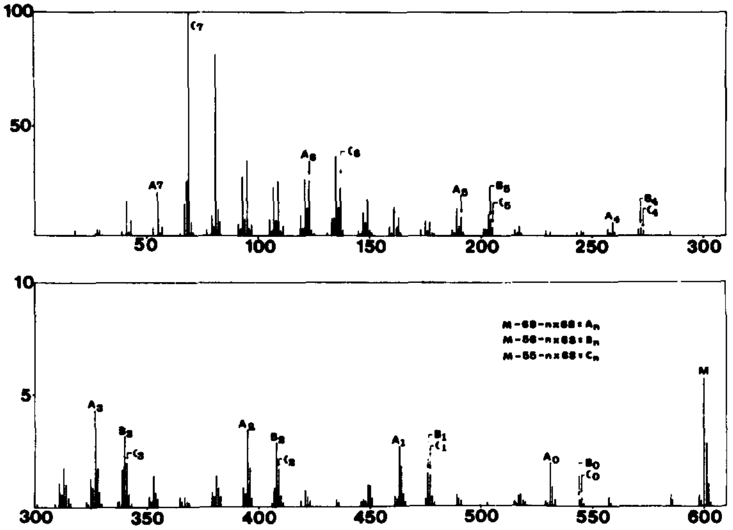
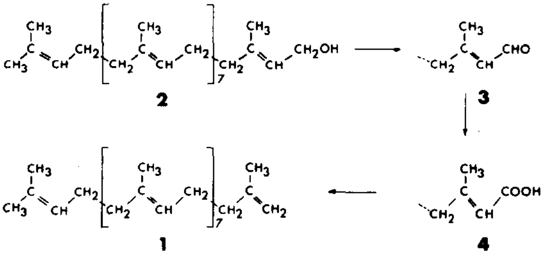


Fig. 1. Mass spectrum of nor-solanesene.

600.5644, required 600.5634), and a set of prominent peaks at M-69-n68 (n = 0-7). The observed fragmentation pattern is characteristic of long chain polyisoprenoids of the general structure $H(-CH_2-C(CH_3)=CH-CH_2-)_nR$[4,5] and suggests that nor-solanesene is made up of eight isoprene units plus a four carbon unit. This is supported by the presence of two other sets of fairly prominent peaks also differring by 68 mass units and due to ions formed by cleavage of the same doubly allylic bonds but involving loss of neutral fragments derived from the end of the chain comprising the four carbon unit, i.e. M-55-n68 (n = 0-7) and M-56-n68 (n = 0-5).

The NMR spectrum (60 MHz, $CDCl_3$, TMS) is also consistent with the above polyisoprenoid structure and shows that the terminal C_4-unit is iso-butenyl. Thus, a multiplet centered at δ 5.16 (8 H) can be assigned to eight protons on trisubstituted olefinic linkages, a resonance peak at δ 4.73 (2 H, $W_{\frac{1}{2}}$ = 3 cps) to a terminal methylene group attached to a quaternary carbon, two fairly narrow and partly overlapping peaks at δ 2.07 and 2.02 (32 H) to 16 allylic in-chain methylene groups, and three partly overlapping peaks at δ 1.72, 1.68 and 1.61 (30 H) to 10 methyl groups attached to olefinic carbons. On the basis of earlier findings[6-8] for related compounds, the position of the last three peaks and corresponding estimated integral values suggest that the peak at δ 1.72 is due to the methyl group attached to the disubstituted double bond, the δ 1.68 peak to the methyl cis to the vicinal olefinic proton and the δ 1.61 peak to the eight methyl groups trans to the corresponding vicinal olefinic protons. Thus these results indicate an all-trans configuration.

The presence of the unsymmetrically-disubstituted double bond and trisubstituted double bonds is confirmed by absorption bands in the infrared at $\nu_{max}^{CCl_4}$ 3078, 1648, 889 ($R,R'C = CH_2$) and $\nu_{max}^{CCl_4}$ 3050, 1665 cm^{-1}, and $\nu_{max}^{CS_2}$ 837 cm^{-1} ($R,R'C = CHR''$), Since the compound shows no absorption in the ultraviolet due to conjugated double bonds and lacks optical rotation, it may be concluded from these results that nor-solanesene possesses the all-head-to-tail structure 1 or



related structures in which one or several of the isoprene units are reversed.

In order to clarify this point, it was decided to synthesize the all-head-to-tail isomer since degradation studies had to be excluded on account of shortage of material. The obvious reason for selecting this isomer was that naturally occurring polyisoprenoids of known structure are head-to-tail linked polymers. Moreover, solanesol (2), of known stereochemistry (all-trans)[7,9], has been isolated from tobacco[10] and could be envisaged as a precursor of nor-solanesene via the corresponding aldehyde (3) and acid (4).

The synthesis was accomplished according to the assumed biogenetic model. Thus solanesol (e.tobacco) on treatment with manganese dioxide in dry acetone at room temperature gave the aldehyde 3[11] (96 %), m.p. 34-35°, $\nu_{max}^{liq.}$ 2764, 2723, 1677, 1631, 1611 cm^{-1}, δ 10.03 (1H,d,J = 8 cps), m/e 628 (M), M-18, M-69-n68 (n = 0-4), M-18-69-n68 (n = 0-6), M-83-n68 (n = 1-4). Oxidation of solanesal with excess neutral Ag_2O in 0.03 molar ethanolic sodium hydroxide under nitrogen for 18 hrs furnished solanesic acid (4, 50 %), m.p. 24-26°, m/e 644 (M), M-44, M-69-n68 (n = 0-4), M-69-44-n68 (n = 0-7), M-99-n68 (n = 1-7), M-100-n68 (n = 1-7). Subsequent decarboxylation of this acid in dry quinoline under N_2 at 200° for 4 hrs using a copper chromite catalyst[8] gave a hydrocarbon (1, 64 %), which was identical in every respect to the naturally occurring nor-compound (IR, NMR, MS, m.p. and mixed m.p. 27-28°). Since solanesol has been synthesized previously[9], the present work formally completes a total synthesis of nor-solanesene.

In view of the co-occurrence of nor-solanesene and solanesol in tobacco, it seems probable that both solanesal and solanesic acid could also be present.

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