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(*E*)-4,8-DIMETHYL-1,3,7-NONATRIENE AND (*E*,*E*)-4,8,12-TRIMETHYL-1,3,7,11-TRIDECATETRAENE, TWO UNUSUAL HYDROCARBONS FROM CARDAMOM OIL

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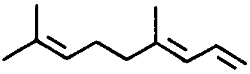
Summary. The identification of two new natural products, (*E*)-4,8-dimethyl-1,3,7-nonatriene 1 and (*E*,*E*)-4,8,12-trimethyl-1,3,7,11-tridecatetraene 3 is reported. These unusual C_{11} and C_{16} hydrocarbons were isolated from the essential oil of *Elettaria cardamomum* Maton var. miniscula Burkhill (Zingiberaceae) and their structures confirmed by synthesis.

In the course of analysis of the commercial essential oil of *Elettaria cardamomum* Maton var. miniscula Burkhill[1], two new constituents, 1 and 3, were isolated by GLC (Carbowax 20 M) of the hydrocarbon fraction[2].

The first compound 1 (ca. 0.09% of the total oil) had a slightly longer retention time on Carbowax columns than terpinolene, a known constituent of this oil[3]. The mass spectrum ($M^{+\cdot}$ at m/z 150) and the ^{1}H-NMR spectrum[4] (18 protons) indicated the empirical formula $C_{11}H_{18}$. In addition, the ^{1}H-NMR spectrum suggested the presence of a 1,1-disubstituted 1,3-butadiene unit, a trisubstituted isolated double bond, 3 olefinic methyl groups, and 4 allylic protons. This leaves the structures 1 and 2 as the only possibilities.



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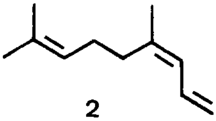

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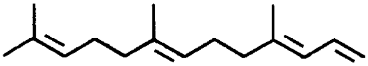
A decision between 1 and 2 based on the ^{1}H-NMR spectrum alone was not possible in the absence of the other isomer. Both compounds were therefore synthesized by the known[5] Wittig reaction of citral (*E*/*Z* ratio 2 : 1) with methylenetriphenylphosphorane (yield 60%). Each isomer (1 : 2 ratio 2 : 1) was isolated by GLC (Carbowax 20 M). The main product (longer retention time) showed the spectral data reported[5,6] for the (*E*)-isomer 1 and was identical (MS, ^{1}H-NMR, GLC) with the natural compound. The minor compound, whose spectra[7] are in agreement with those reported for the (*Z*)-isomer 2[5,6], could not be detected in cardamom oil.

The second compound 3 (ca. 0.17%) was the last peak (Carbowax 20 M) of the hydrocarbon fraction and its retention time was between that of geranyl acetate and geraniol. The mass spectrum ($M^{+\cdot}$ at m/z 218) and the ^{1}H-NMR spectrum[8] (26 protons) suggested the empirical formula

$C_{16}H_{26}$. Some of the ^{1}H-NMR signals were very similar to those of 1, but additional signals indicated the presence of one more isoprene unit. This led to the hypothetical structure 3,



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which was corroborated by the ^{13}C-NMR spectrum[8]. In particular, the (*E*,*E*)-configuration followed unambiguously from the ^{13}C chemical shifts of the methyl groups. The 3 quadruplets at higher field (16.0 - 17.7 ppm) must be assigned to methyl groups which are *cis* to the main chain, whereas the signal at 25.7 ppm is at a typical position for a *trans* methyl group.

The compound 3 was synthesized by the Wittig reaction of farnesal[9] with methylenetriphenylphosphorane (yield 80%, b.p. 120 - 130°/0.2 Torr). The main peak (eluted last) of the mixture of the four geometric isomers was isolated by GLC (Carbowax 20 M) and found to be identical (GLC, ^{1}H-NMR) with the natural compound.

REFERENCES AND NOTES

1. S. Arctander, 'Perfume and Flavor Materials of Natural Origin', Elizabeth N.J. (U.S.A), 1960, p. 126; E. Gildemeister & F. Hoffmann, "Die ätherischen Oele", Vol. 4, Akademie-Verlag, Berlin, 1961, p. 496.
2. Ca. 10%, obtained by liquid chromatography of the essential oil on silica gel with hexane.
3. B.M. Lawrence, Perfumer & Flavorist 8 (4), 63 (1983), and references cited therein.
4. ^{1}H-NMR (360 MHz, $CDCl_3$): δ 1.61 (3 H, *s*), 1.68 (3 H, *s*), 1.76 (3 H, *s*), 2.04 - 2.15 (4 H, *m*), 4.98 (1 H, b*d*, *J* = 10 Hz), 5.10 (1 H, b*d*, *J* = 17 Hz), 5.11 (1 H, *t*, partly covered), 5.86 (1 H, b*d*, *J* = 10 Hz), 6.58 (1 H, *td*, *J* = 10 and 17 Hz).
   ^{13}C-NMR (90.5 MHz, $CDCl_3$): δ 16.7 (*q*), 17.7 (*q*), 25.7 (*q*), 26.6 (*t*), 39.7 (*t*), 114.6 (*t*), 124.0 (*d*), 125.5 (*d*), 131.7 (*s*), 133.5 (*d*), 139.6 (*s*). MS *m/z* (rel. intensity): 69 (100), 41 (41), 81 (17), 79 (15), 39 (10), 67 (9), 53 (9), 82 (8), 150 (7), 107 (7), 135 (6), 77 (5). IR (neat): 3090, 3040, 1650, 1600, 1450, 1420, 1385, 990, 900 cm^{-1}. UV (EtOH) λ_{max} (log ε) 235 nm (4.60).
5. G. Pattenden & B.C.L. Weedon, J. Chem. Soc. (C) 1968, 1984.
6. L. Barlow & G. Pattenden, J.Chem. Soc. Perkin I 1976, 1029.
7. ^{1}H-NMR (360 MHz, $CDCl_3$): δ 1.61 (3 H, *s*), 1.68 (3 H, *s*), 1.78 (3 H, *s*), 2.09 (2 H, *m*), 2.18 (2 H, *m*), 4.95 (1 H, b*d*, *J* = 10 Hz), 5.07 (1 H, b*d*, *J* = 17 Hz), 5.12 (1 H, *t*, partly covered), 5.86 (1 H, b*d*, *J* = 10 Hz), 6.57 (1 H, *td*, *J* = 10 and 17 Hz).
   ^{13}C-NMR (90.5 MHz, $CDCl_3$): δ 17.7 (*q*), 23.8 (*q*), 25.7 (*q*), 26.8 (*t*), 32.5 (*t*), 114.4 (*t*), 124.0 (*d*), 126.4 (*d*), 132.0 (*s*), 133.2 (*d*), 139.8 (*s*). MS: 69 (100), 41 (42), 79 (19), 107 (18), 81 (15), 135 (10), 67 (10), 53 (10), 39 (10), 150 (7), 82 (7), 77 (7).
   IR (neat): same bands as for 1. UV (EtOH) λ_{max} (log ε) 236 nm (4.44).
8. ^{1}H-NMR (360 MHz, $CDCl_3$): δ 1.60 (6 H, *s*), 1.68 (3 H, *s*), 1.77 (3 H, *s*), 1.98 (2 H, *m*), 2.03 - 2.16 (6 H, *m*), 4.98 (1 H, b*d*, *J* = 10 Hz), 5.07 - 5.13 (3 H, *m*), 5.86 (1 H, b*d*, *J* = 10 Hz), 6.58 (1 H, *td*, *J* = 10 and 17 Hz).
   ^{13}C-NMR (90.5 MHz, $CDCl_3$): δ 16.0 (*q*), 16.7 (*q*), 17.7 (*q*), 25.7 (*q*), 26.4 (*t*), 26.8 (*t*), 39.7 (*t*), 39.9 (*t*), 114.6 (*t*), 123.9 (*d*), 124.4 (*d*), 125.5 (*d*), 131.4 (*s*), 133.5 (*d*), 135.4 (*s*), 139.6 (*s*). MS: 69 (100), 81 (43), 41 (25), 79 (10), 53 (9), 67 (8), 94 (8), 95 (7), 68 (7), 82 (6), 70 (6), 55 (6). IR (neat): same bands as for 1. UV (EtOH) λ_{max} (log ε) 236 nm (4.16).
9. Prepared from commercial farnesol with pyridinium chlorochromate. The product is a mixture of the four stereoisomers with the (*E*,*E*)-isomer (eluted last) prevailing.

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