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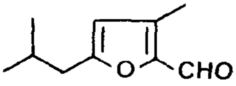
5-ISOBUTYL-3-METHYL-2-FURANCARBALDEHYDE, A NEW MONOTERPENOID FROM THE ESSENTIAL OIL OF *TAGETES GLANDULIFERA* SCHRANK

Bruno Maurer* and Arnold Hauser

Firmenich SA, Research Laboratories, 1211 Geneva 8, Switzerland

Summary: The new monoterpenoid 5-isobutyl-3-methyl-2-furancarbaldehyde was isolated from *Tagetes glandulifera* Schrank and its structure confirmed by synthesis.

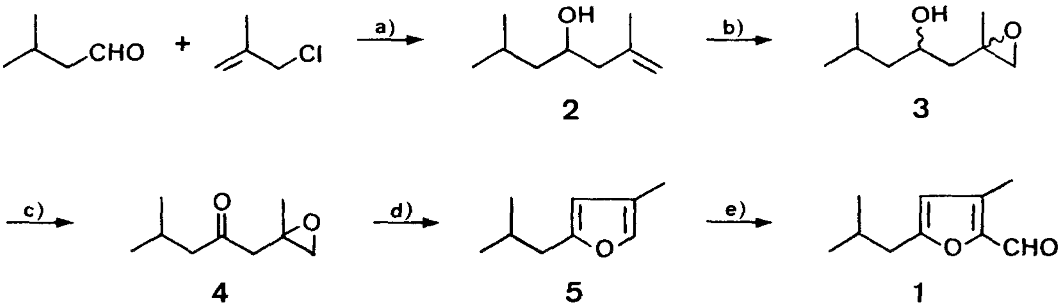
In the course of analysis of the essential oil of *Tagetes glandulifera* Schrank[1] a new compound (ca. 0.1%; slightly more polar than (*Z*)-ocimenone, a well-known constituent of this oil[2]) was isolated by chromatography on silica gel and gas chromatography. The mass spectrum ($M^{+\cdot}$ at m/z 166) and the ^{1}H-NMR spectrum (14 protons) indicated the empirical formula $C_{10}H_{14}O_2$. In addition, the ^{1}H-NMR spectrum[3] also suggested the presence of a methyl group, an isobutyl group, and an aldehyde function, all attached to a furan ring; the β-position of the furyl proton was indicated by its chemical shift (6.07 ppm). On these grounds and for biogenetic reasons (two head-to-tail linked isoprene units) structure 1, a new type of a highly oxidized regular monoterpene, was postulated.



1

This hypothesis was confirmed by synthesis (*Scheme*).

Scheme



a) Mg, ether/10 - 15°, 3 h; b) MCPBA, CH_2Cl_2/25°, 5 h; c) PDC, CH_2Cl_2/25°, 15 h;
d) 2 N H_2SO_4, pentane/25°, 1 h; e) $POCl_3$, DMF/15 - 25°, 4 h.

The Barbier reaction[4] between methylallyl chloride and isovaleraldehyde in ether gave alcohol 2[5] (b.p. 68 - 69°/12 Torr, yield 92%) which was epoxidized with m-chloroperbenzoic acid to give epoxy-alcohols 3 (b.p. 30 - 39^{0}/0.02 Torr, yield 89%, mixture of diastereomers). Oxidation of 3 with pyridinium dichromate[6] yielded the epoxy-ketone 4 (b.p. 33 - 34^{0}/0.02 Torr, 75% yield) which on treatment with acid rearranged[7] to the furan 5[8] (b.p. 55 - 56^{0}/ 20 Torr, yield 72%). Vielsmeier formylation of 5 gave aldehyde 1 (b.p. 80 - 90^{0} (bath)/ 0.02 Torr, yield 93%), identical with the natural product by NMR, MS and GLC.

References and Notes

1. S. Arctander, 'Perfume and Flavor Materials of Natural Origin', Elizabeth N.J. (U.S.A.), 1960, p. 606; E. Gildemeister & F. Hoffmann, "Die ätherischen Oele", Vol. 7, Akademie-Verlag, Berlin, 1961, p. 627.
2. D.J.J. de Villiers, C.F. Garbers & R.N. Laurie, Phytochemistry 10, 1359 (1971).
3. NMR (360 MHz, $CDCl_3$): δ 0.95 (6 H, d, J = 7 Hz), 2.04 (1 H, m, J = 7 Hz), 2.33 (3 H, s), 2.53 (2 H, d, J = 7 Hz), 6.07 (1 H, s), 9.64 (1 H, s). MS m/z (rel. intensity): 124 (100), 123 (78), 166 (60, $M^{+\cdot}$), 41 (34), 43 (28), 95 (25), 39 (22), 67 (19), 65 (12), 125 (8), 66 (8), 167 (7). IR (neat): 2850, 2760, 1680, 1605, 1535, 1480, 1435, 1400, 1300, 1005, 780 cm^{-1}. UV (EtOH) λ_{max} (log ε) 237 (3.1), 290 nm (4.4).
4. C. Blomberg & F.A. Hartog, Synthesis 1977, 18.
5. All new compounds exhibited satisfactory spectral data (^{1}H-NMR, MS, IR).
6. E.J. Corey & G. Schmidt, Tetrahedron Letters 1979, 399.
7. R.A. Cormier & M.D. Francis, Synth. Commun. 11, 365 (1981).
8. NMR (360 MHz, $CDCl_3$): δ 0.92 (6 H, d, J = 6.5 Hz), 1.92 (1 H, m), 1.98 (3 H, d, J = 1 Hz), 2.43 (2 H, d, J = 7 Hz), 5.84 (1 H, br. s), 7.05 (1 H, qi, J = 1 Hz). MS m/z (rel. intensity): 95 (100), 138 (33, $M^{+\cdot}$), 96 (11), 67 (9), 41 (8), 39 (5), 139 (3), 65 (3), 123 (2), 43 (2). IR (neat): 1620, 1550, 1465, 1390, 1370, 1130, 800 cm^{-1}.

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