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MALVACEAE

ISOLATION OF BISABOLENE OXIDE FROM THE COTTON BUD*

P. A. HEDIN, A. C. THOMPSON and R. C. GUELDNER
Entomology Research Division, Agricultural Research Service, USDA
State College, MS 39762, U.S.A.

and

J. M. RUTH
Entomology Research Division, Agricultural Research Service, USDA
Beltsville, MD 20705, U.S.A.

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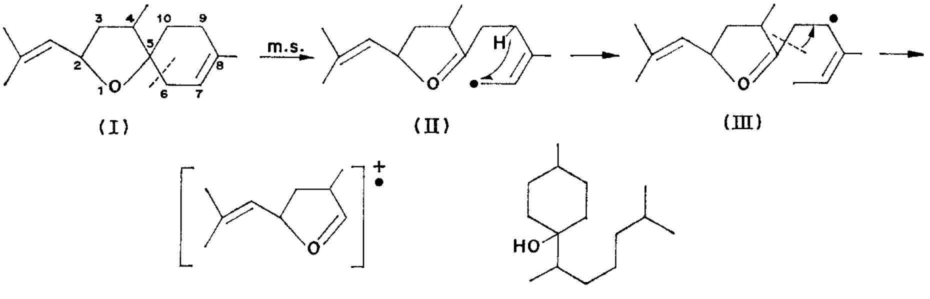
We report the isolation of a new sesquiterpene oxide [4,8-dimethyl-2-(2-methylpropenyl)-1-oxaspiro[4·5]dec-7-ene] (I) from the essential oil of the cotton plant (*Gossypium hirsutum* L. var. Deltapine Smooth Leaf), and propose the trivial name, bisabolene oxide.



(I) (II) (III)

(IV) (V)

The structural assignment is based on MS, PMR, UV, and IR evidence and on reduction of the compound with chloroplatinic acid to tetrahydro-β-bisabolol (V).[1] Carbonyl functionality is rejected because of the absence of UV absorption above 220 nm and because it was unaltered by reduction with sodium borohydride or lithium aluminum hydride. The IR absorptions at 1020 and 1060 cm^{-1} suggest the presence of ether type C—O—C bonds. No terminal methylene absorption was present. High resolution mass spectrometry requires $C_{15}H_{24}O$. Double allylic fission gives *m/e* 138, $C_9H_{14}O$ (IV), the most abundant fragment. PMR analysis requires 2 vinyl hydrogens, 3 vinyl methyls, and one methyl split by a methinyl proton. One of the carbons (C-5) of the oxygen bridge is fixed from the isolation of tetrahydro-β-bisabolol. Carbons C-4, C-6, and C-10 are eliminated as the other bridge carbon

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[1] J. P. MINYARD, A. C. THOMPSON and P. A. HEDIN. *J. Org. Chem.* 33, 909 (1968).

because of the stability of the compound in $LiAlH_4$, and C-4 by the requirement for a methyl split by a methinyl proton. Attachments to C-8 and the methyl at C-8 are rejected because of the vinyl methyl requirement. Attachments at C-3 and C-9 are rejected because of the requirement for *m/e* 138 and the anticipated instability of 4-membered-oxygen containing rings to reduction. C-7 is eliminated for the same reason plus the requirement for a vinyl proton on this carbon. Attachment at C-2 is compatible with the requirement for a vinyl proton on the isobutenyl side chain and the methinyl proton resonance at 3·11 ppm.*

EXPERIMENTAL

Isolation of bisabolene oxide I. Chromatography of 30 ml cotton essential oil on Florisil yielded a mixture containing the desired compound in the fraction eluting with 2% Et_2O in pentane. The desired compound, an oil with a pleasant apple floral odor, was subsequently obtained by refluxing in Et_2O with $LiAlH_4$ to remove several ester and epoxide contaminants and then subjected to preparative TLC on silica gel G with 2% Et_2O in pentane. The isolation was monitored by TLC. The component gave a cherry-red spot when the plate was heated at 100° for 3–5 min after spraying with 3% vanillin in 0·5% conc H_2SO_4 in MeOH. Preparative GLC was abandoned because of marked degradation. Yield from 30 ml cotton oil: 60 mg. Percentage of cotton oil: 0·2%.

Chromatographic data. $I_kC_{20}M$: 1785 (0·51 mm × 15·24 m SCOT silanized column coated with 20% Carbowax 20M, carrier gas flow 1·0 ml/min He_2, column temp. 125°). I_k XE-60: 1530 (0·032 × 3 m column packed with 15% XE-60 on 60/80 Gas Chrom Q, carrier gas flow 40 ml/min N_2, column temp. 150°). R_f SGG, ethyl ether–pentane: 10/90; 0·80.

MS. (70 ev) *m/e* 138 (100), 96 (59), 109 (56), 41 (52), 95 (50), 115 (40), 67 (35), 117 (35), 220 (40) = molecular ion. High resolution mass measurement: 220·1826; $C_{15}H_{24}O$ requires 220·1827. 138·1044, $C_9H_{14}O$ requires 138·1045.

PMR. Analysis in CCl_4 showed ppm (δ) 0·90 d (3) $\underline{CH_3}CHR'R''$, 1·20 s, br (2) $R'R''R'''\underline{CH_2}R''''$(C-10), 1·55 s (9) vinyl methyls, 1·35–2·20 m (7) methylenes and methinyl, 3·11 m (1) $R'R''\,\underline{CH}\,OR'''$, 4·92 s, br (1) $R'R''C{=}\underline{CH}\,R'''$, 5·07 s br (1) $R'CH_3C{=}\underline{CH}R''$.

IR. Analysis in CCl_4 included ν_{max} 1020 (s), 1060, 1250 (w), 1370, 1445 (s), 1729 (w), 2920 (s), 2990 (w) cm^{-1}. There was no UV absorption above 217 nm.

Hydrogenation of bisabolene oxide to tetrahydro-β-bisabolol (V). The compound was hydrogenated with chloroplatinic acid in *iso*PrOH at room temp. and atmospheric pressure. Completeness of the reaction was determined by TLC and GLC. The product was collected by preparative GLC from a 0·0064 × 1·220 m Carbowax 20M column at 150°. I_k: 1840.

MS. 113 (100), 95 (53), 123 (44), 124 (44), 41 (38), 81 (31), 55 (29), 43 (28), 110 (22), 208 (9), 226 (1) = molecular ion, nearly identical to that of Minyard *et al.*:[1] 113 (100), 95 (44), 124 (17), 123 (13), 81 (12), 41 (7), 55 (7), 208 (3), 226 (1). High resolution mass measurement: 226.2308, $C_{15}H_{30}O$ requires 226·2297. 113·0973 and 113·1321. $C_7H_{13}O$ requires 113·0966, C_8H_{17} = 113·1330. Metastable at 79·9, $113^{-}H_2O95$. $(95)^2/113 = 79{\cdot}9$.

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* Synthesis for confirmation in progress as a M.S. thesis by N. V. Moody under the direction of D. H. Miles, Department of Chemistry, Mississippi State University, State College.

Key Word Index—Gossypium hirstum; Malvaceae; sesquiterpene; 4,8-dimethyl-2-(2′-methylpropenyl)-1-oxaspiro[4-5]dec-7-ene; bisabolene oxide.