Phytochemistry, 1971, Vol. 10, pp. 1693 to 1694. Pergamon Press. Printed in England.

MALVACEAE

ISOLATION OF α-BISABOLOL FROM THE COTTON BUD*

P. A. HEDIN, A. C. THOMPSON and R. C. GUELDNER
Entomology Research Division, Agricultural Research Service, U.S. Department of Agriculture, State College, Mississippi 39762, U.S.A.

and

J. P. MINYARD
Mississippi State Chemical Laboratory, Mississippi State University, State College, Mississippi 39762, U.S.A.

(*Received* 20 *October* 1970)

THE ISOLATION of β-bisabolol[1-(1,5-dimethyl-4-hexenyl-)-4-methyl-3-cyclohexen-1-ol] from the essential oil of the cotton plant (*Gossypium hirsutum* L. var. Deltapine Smoothleaf) was reported previously.[1] A further investigation of the fraction yielding β-bisabolol[2] resulted in the isolation of another sesquiterpene alcohol present in lower concentration (0·6% of the oil) which now has been shown to possess the same physical, PMR and IR properties as α-bisabolol (6-methyl-2 (4-methyl-3-cyclohexen-1-yl)-5-hepten-2-ol) isolated from Oil of Chamomile German Extra. The PMR spectra of tetrahydro-α-bisabolol furthur supports the structural assignment. It was not possible to isolate a sufficient quantity of α-bisabolol from cotton oil for determination of optical activity, but the absolute configuration may be different from that of the (−)-α-bisabolol of chamomile oil, since mass analysis gave spectra similar to β-bisabolene for the former, but α-bisabolene for the latter. This is the first report of the occurrence in Malvaceae of α-bisabolol which previously had been isolated from *Populus balsamifera* L.[3] and chamomile oil[4] (*Matricaria chamomilla* L.). The cotton essential oil also contains γ-bisabolene[5] and a partially characterized bisabolene oxide which yields tetrahydro-β-bisabolol when hydrogenated.

EXPERIMENTAL

Isolation of α-Bisabolol

Chromatography of 50 ml cotton essential oil and 10 ml chamomile oil on Florisil yielded a mixture containing the desired compound in the fraction eluting with Et_2O–pentane (5:95). The desired compound, a yellow-brown oil, was subsequently obtained by pre parative TLC on silica gel-G with Et_2O–pentane (5:95), or, alternately, by preparative GLC on a 6·4 mm × 3·047-m column packed with 28·5% C_{20M} on HMDS-treated chromosorb P, 60/80 mesh. Carrier gas flow N_2 was 140 ml/min; column temperature 160°, injector 170°, detector 180°. Yield from cotton oil: 280 mg; yield from chamomile oil: 560 mg. The optimal rotation was not determined.

* Mention of a proprietary product in this paper does not constitute an endorsement of this product by the U.S. Department of Agriculture.

[1] J. P. MINYARD, A. C. THOMPSON and P. A. HEDIN, *J. Org. Chem.* **33**, 909 (1968).
[2] J. P. MINYARD, D. D. HARDEE, R. C. GUELDNER, A. C. THOMPSON, G. WIYGUL and P. A. HEDIN, *J. Agri. Food Chem.* **17**, 1093 (1969).
[3] F. SORM, M. VRANY and V. HEROUT, *Chem. Listy* **46**, 364 (1952).
[4] F. SORM, M. ZAORAL and V. HEROUT, *Coll. Czech. Chem. Commun.* **16**, 626 (1951).
[5] J. P. MINYARD, J. H. TUMLINSON, A. C. THOMPSON and P. A. HEDIN, *J. Agri. Food Chem.* **14**, 332 (1966).

Chromatographic data for both isolates. $I_k^6C_{20M}$: 2022, I_k SE-30: 1595 (10% SE-30 on HMDS-treated Chromosorb P, 60/80 mesh, column temperature 175°). R_f: SGG, ethyl ether/pentane: 10/90; 0·40.

Mass spectrum cotton oil isolate m/e 69 (100), 41 (34), 43 (30), 109 (30), 119 (29), 81 (27), 93 (26), 135 (15), 204 (12), 222 (0·5). Similarity to β-bisabolene:[7] 69 (100), 41 (82), 93 (77), 204 (20).

Mass spectrum chamomile oil isolate m/e 93 (100), 109 (69), 41 (65), 43 (57), 204 (56), 121 (43), 95 (35), 222 (0·5). Similarity to α-bisabolene:[7] 93 (100), 41 (34), 121 (28), 204 (18).

PMR spectrum of both isolates. PMR analysis in CCl_4 showed ppm (δ) 1·15 t (3, 10·5) RR′CH—CH_3 1·48 s (1) —OH; 1·62 d (9) vinyl methyls; 1·77–2·15 (8) methylenes; 2·22 s, br (1) R′R″CHR‴; 2·34 m, br (2) R′R″C =CHCH_2 R‴; 5·10 s (1) RCH = C CH_3 CH_3; and 5·35 s (1) R′ CH_3C = CHR″.

IR spectrum of both isolates. The IR spectrum in CCl_4 included ν_{max} 793, 810, 910, 1010, 1100, 1145, 1255, 1280, 1370, 1445, 1715 (sl) 2910, and 3440 cm^{-1}. The spectrum was essentially identical to that determined by Pliva *et al.*[8]

Hydrogenation of α-bisabolol to tetrahydro-α-bisabolol. α-Bisabolol was hydrogenated with chloroplatinic acid in isopropanol at room temp. and atmospheric pressure. Completeness of the reaction was determined by TLC and GLC.

PMR spectrum. PMR analysis in CCl_4 showed ppm (δ) 0·82 s (1) —OH; 0·94 d (6, 5·0) RCH CH_3 CH_3; 0·96 d (3, 5·0) R′R″CHCH_3; 1·21 m (2); 1·28 s (3) R′R″COHCH_3; 1·15–1·50 s br (12) methylenes; 1·50–1·90 s, br (3) R′R″CH C—OH—CH_3R‴ and R′CH_2 C—OH—CH_3R″.

IR spectrum. The IR spectrum in CCl_4 included ν_{max} 790, 810, 830, 915, 980, 1000, 1090, 1165, 1240, 1360, 1445, 1540, 1690, 2890, 3370 $cm.^{-1}$

[6] E. sz. KOVÁTS, *Z. Anal. Chem.* **181,** 351 (1961).
[7] Y. HIROSE, *Shitsuryo Buneski* **15,** 162 (1967).
[8] J. PLIVA, M. HORAK, V. HEROUT and F. SORM, *Die Terpene, Teil I: Sesquiterpene* S 16, 17 Akademie Berlin (1960).