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MALVACEAE

CONSTITUENTS OF THE COTTON BUD*

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Abstract—The investigation of the alcohol fraction of the essential oil of cotton (*Gossypium hirsutum* L. var. Deltapine Smoothleaf) with an integrated gas-liquid chromatography-mass spectrometry system resulted in the identification of 17 additional alcohols and β-ionone. Tentative assignments were made for 4 other alcohols. None of these has previously been reported in cotton.

INTRODUCTION

THE ISOLATION of β-bisabolol[1] and α-bisabolol[2] from the essential oil of the cotton plant (*Gossypium hirsutum* L. var. Deltapine Smoothleaf) were previously reported. A further investigation of the alcohol fraction with an integrated gas chromatography–mass spectrometry system resulted in the identification of 17 additional alcohols and β-ionone. Tentative assigments were made for 4 other alcohols. At least 2 acyclic terpene alcohols were also present (Table 1). This report is apparently the first concerning volatile alcohols other then the bisabolols in the cotton plant.

The alcohol fraction comprises about 16·3 per cent of the total essential oil, 34·3 per cent of which is β-bisabolol. No other major alcohol is present, *cis*-3-hexen-1-ol (5·6%), *trans*-2-hexen-1-ol (5·5%), 1-penten-3-ol (3·4%), and 6-octen-4-ol (3·0%) being the next most abundant. The study was made partly to determine whether the alcohol fraction of the cotton essential oil contained apparent precursors to the 4 C_{10} components of the attractant-aggregant pheromone of the male boll weevil, *Anthonomus grandis* Boheman.[3] Since the male must have a diet of fresh cotton before he can produce the pheromone, 2-methyl-6-methylene-2-octen-8-ol was proposed as a common precurson of all 4 com ponents.[4] Some support for this possibility was provided by the presence of 2 acyclic C_{10} alcohols (4·5 and 2·7 per cent), whose structures could not be assigned from the mass spectral data. A reinvestigation of the unidentified C_{10} alcohols with a more efficient column and the extension of this work to the remaining C_{15} alcohols is therefore indicated.

EXPERIMENTAL

Column chromatography. The cotton essential oil (3 g quantities) was chromatographed on 2 × 25-cm Florisil[5] column. The hydrocarbons were eluted with pentane, the carbonyls, esters, and oxides with 2% Et_2O in pentane, and the alcohols with 10% Et_2O in pentane. Progress was monitored by silica gel TLC.

* Part XXI in the series "Constituents of the Cotton Bud". For Part XX see Ref. 2.

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

TABLE 1. ANALYSIS OF THE ALCOHOL FRACTION OF THE COTTON ESSENTIAL OIL

Compound	I_k C 20M*	MS fragmentation†	Ref.	%‡
Isoamyl alcohol	1137	—		2·5
2-Methylbutanol	1158	—		1·5
3-Methylbutanol	1175	55,41,42,43,70; 88	7	0·1
l-Pentanol	1246	42,55,41,43,70; 88	7,8	1·5
—	1265	—		0·6
l-Penten-3-ol	1301	57,45,67,41,43; 86	8	3·4
trans-2-Hexen-l-ol	1330	57,41,43,39,44; 100	7,8	5·5
l-Hexanol	1355	56,43,55,42,41; 102	7,8	1·0
cis-3-Hexen-l-ol	1378	41,67,55,82,69; 100	7,8	5·6
4-Hexen-l-ol	1415	—		0·8
Cyclohexanol	1445	57,67,41,43,82; 100	7	0·6
Linalool + C_{15}HC	1597	43,41,55,71,69; 154	7,8,9	0·6
6-Octen-4-ol	1648	43,55,45,41,99; 128	—	3·0
—	1630	—	—	1·0
Acyclic C_{10} alcohol	1682	41,43,55,57,95; 154	—	2·7
alpha-Terpineol	1698	59,93,43,41,121; 154	7,8,9	4·9
Acyclic C_{10} alcohol	1718	41,43,55,82,57; 154	—	4·5
Isoborneol	1732	95,71,110,43,55; 154	7,8,9	1·1
Citronellol	1765	41,69,43,55,67; 156	7,8,9	2·0
Carveol	1778	119,91,41,43,134; 152	7	1·6
Nerol	1800	41,69,55,43,67; 154	8,9	2·4
—	1819	—	—	0·3
Geraniol	1836	—	7,8,9	0·2
Benzyl alcohol	1870	79,77,108,107,55; 108	8	0·3
2-Phenylethanol	1908	91,92,41,39,65; 122	8	1·1
—	1930	—	—	0·1
β-Ionone	1946	43,41,177,135,55; 192	8	0·6
—	1970	—	—	0·2
tert-C_{15} alcohol	1980	41,43,55,69,79; 222	—	1·2
Nerolidol	2055	69,41,43,93,55; 222	8	0·8
Monocyclic C_{15} alcohol	2145	82,41,43,93,111; 222	—	3·3
Sub-total				57·1
β-Bisabolol				34·3
α-Bisabolol				0·6
Unidentified sesquiterpene alcohols and other				8·0
Total				100·0

* E. sz. KOVÁTS, *Analyt. Chem.* **181**, 351 (1961).

† The five most intense fragment ion values (*m/e*) arranged in order of decreasing relative abundance with the proposed parent ion presented 6th.

‡ Per cent of total alcohol fraction.

Preparative GLC. The alcohol fraction was further fractionated on a 1·22 m × 6·4 mm column packed with 28·5% Carbowax 20M on HMDS-treated Chromosorb P, 60/80 mesh. Carrier gas flow was 175 ml/min N_2, column temperature 160°, injector 170°, detector 180°. Three gross consecutive fractions were collected which corresponded approximately to the C_5 and C_6 alcohols, the monoterpene alcohols, and the sesquiterpene alcohols. Analytical GLC and TLC were employed to assure the integrity of the collected fractions. The C_5 and C_6 alcohols were then chromatographed on a 3·0 m × 6·4 mm column packed with 20% Carbowax 20M on HMDS-treated Chromosorb P, 60/80 mesh. Carrier gas flow N_2 was 50 ml/min, column temperature 110°, injector 170°, detector 185°. Individual peaks were trapped and sealed for mass spectrometric analysis. Before the alcohol fractions were investigated by GLC–MS, 6-m C_{4000} columns were used to trap sufficient quantities for NMR and IR analysis. Only 1-hexanol, *cis*-3-hexen-1-ol and *trans*-2-hexen-1-ol were identified in this manner.

Analytical GLC-MS. The C_5 and C_6 alcohols which had been trapped individually were introduced into the MS by direct inlet. The gross C_{10} fraction (0·2 μl of the neat oil) was introduced via a Watson-

Biemann separator from a 15·24 m × 0·25 mm SCOT silanized column coated with 20% Carbowax 20M. Carrier flow was 1·0 ml/min N_2, column temperature 125°. The mass spectrometer was a double focusing PE-270 unit. Approximate material balances for all fractions were obtained by weighing or peak triangulation as appropriate. GLC retention times are presented as Kovâts[6] indices (I_k). Fragment ion values were compared with those of Cornu and Massot[7], Bondarovich *et al.*,[8] and von Sydow.[9]

6-*Octen*-4-*ol*. The Kovâts indices were consistent with this assignment. The suggested analysis by MS was as follows: McLafferty rearrangement of the parent results in the elimination of ethylene; subsequent abstraction of a proton gives *m/e* 99. Alpha fission of the carbon adjacent to oxygen of *m/e* 128 yields *m/e* 43 and 55. Location of the vinyl group at C_6 reinforces *m/e* 55. *M/e* 45 arises from *m/e* 100 (*m/e* 99).

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NYCTAGINACEAE

CONSTITUENTS OF ROOTS OF *BOERHAAVIA DIFFUSA*

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Abstract—Hentriacontane, β-sitosterol and ursolic acid have been isolated from roots of *Boerhaavia diffusa* (Linn).

Plant. Boerhaavia diffusa (Linn).

Occurrence. Distributed in tropical and sub-tropical regions. Six species are found in India.

Uses. The root of the plant is considered laxative and diuretic. It has also expectorant properties and is used in asthma.[1] In large doses, it acts as an emetic. Powder of the plant is used in abdominal tumors[2] and cancer.[3]

Previous work. Pharmacological studies of an alkaloid[4] and an acid[5] of unknown structure reported.

Roots. Extracted with light petroleum (60–80°) and chromatographed on Brockmann Alumina.

Hentriacontane. $C_{31}H_{64}$ (found: C, 84·50; H, 14·62; required: C, 84·97; H, 15·03, m.p., mixed m.p., IR and NMR) earlier petroleum fractions and crystallizations (hexane).

Ketone. (m.p. 86°, IR 1725). Hindered, no DNP or oxime derivative. Oxidation with conc. HNO_3 gives an acid (IR). Further work is in progress. From later petroleum fractions and crystallization ($CHCl_3$–MeOH).

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