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LACINILENE C, A REVISED STRUCTURE, AND LACINILENE C 7-METHYL ETHER FROM *GOSSYPIUM* BRACTS*

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Key Word Index—*Gossypium hirsutum*; Malvaceae; cotton; sesquiterpenes; revised structure; cadinane skeleton; lacinilene C and its 7-methyl ether.

Abstract—Two sesquiterpenes, which exhibit brilliant yellow fluorescence in the ultraviolet, have been isolated from frost-killed cotton bracts. They have been identified as lacinilene C and its 7-methyl ether. A revised structure related to the cadinane ring system is proposed for lacinilene C.

INTRODUCTION

Desiccated bract tissue, the leaf-like structure subtending the boll of the cotton plant (*Gossypium hirsutum* L.) is a prominent constituent of the "cotton dust" generated during cotton fiber processing. Aqueous extracts of dried cotton bracts have been reported to induce the symptoms of byssinosis in susceptible persons [1, 2], and phenolic plant pigments have been suggested as the active agents [2]. We report here the isolation and identification of two water-soluble pigments in frost-killed bracts that were not found in leaf, stem, or root tissue (unpublished data). The biological activity of these compounds has not yet been studied.

RESULTS AND DISCUSSION

Two yellow fluorescent pigments were noted (365 nm UV light) when aqueous extracts from desiccated bracts were chromatographed on silica gel plates with Et_2O. High-resolution MS showed that the slower moving pigment was a sesquiterpene ($C_{15}H_{18}O_3$). The IR spectrum (KBr) indicated the presence of a conjugated ketone (1645, 1610 cm^{-1}). A positive $FeCl_3$ test and a large bathochromic shift (73 nm) in the UV spectrum upon addition of base to an EtOH solution showed that a phenol group is apparently conjugated with this ketone. An isopropyl group appeared in the NMR spectrum as a doublet of doublets centered at δ 1·25 (J 6·6, 6H), with a chemical shift difference of 1·5 cps. It was coupled (shown by spin decoupling) with a multiplet centered at δ 3·15 (1H). The position of this methine indicated bonding to a sp^2-carbon. Two other methyl groups appeared as singlets, an aromatic methyl group at δ 2·22 (3H) and a deshielded methyl group at δ 1·50 (3H). A vinyl singlet was observed at δ 5·91 (1H, OC–CH=C), and two aromatic protons appeared as singlets at δ 7·04 (1H) and δ 7·22 (1H). Because of small sample size and the diffuse nature of the peaks, the phenolic proton and another hydroxyl proton were not observed, but they were clearly indicated in the IR spectrum (3050–3550 cm^{-1}).

The isolation of lacinilene C from *Ulmus laciniata* Mayr. was recently reported [3]. Structure (**1**) was proposed for this compound. The mp, NMR and MS spectra of the slower moving pigment from cotton agreed well with those of lacinilene C, and the IR spectra of the two compounds were identical, indicating that they are the same.

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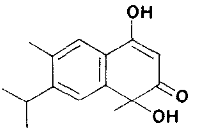
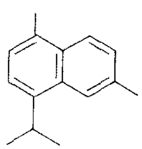
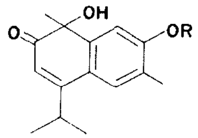
We propose that lacinilene C is 1,7-dihydroxy-4-isopropyl-1,6-dimethyl-2-(1H)-naphthalenone **(3)** rather than **(1)**. Sesquiterpenes derived from cadalene **(2)** are well known in *Gossypium* species and in *U. laciniata*, but terpenes resembling structure **(1)** have not previously been observed in nature. The spectral data on lacinilene C [3] does not exclude a cadinane type of structure. Spectral data supports structure **(3)** since it explains the appearance of a doublet of doublets for the isopropyl methyl group. That is, a chemical shift difference of 1·5 cps is of the magnitude expected for an isopropyl group separated from an asymmetric center by four bonds [4]. A UV bathochromic shift of 73 nm is expected for a phenol group situated in a position *para*-vinylogous to a carbonyl group in changing from a neutral to a basic solution [5].



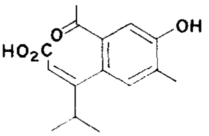
(1)



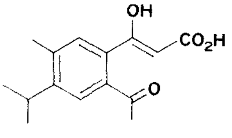
(2)



(3) R = H
(4) R = Me



(5)



(6)

The mass spectral fragmentation of lacinilene C also may be assigned to structure **(3)** as in Fig. 1. Structure **(3)** agrees with the chemical data on lacinilene C [3]. Compound **(3)** would give a diacetate. On oxidation with sodium periodate **(3)** would produce a methyl ketoacid **(5)** that is different from the acid **(6)** reported by Suzuki *et al.* [3]. However, **(5)** does agree with the spectral data given by these workers for **(6)**. The collected data (biogenetic, chemical and spectral) indicate lacinilene C has structure **(3)**.

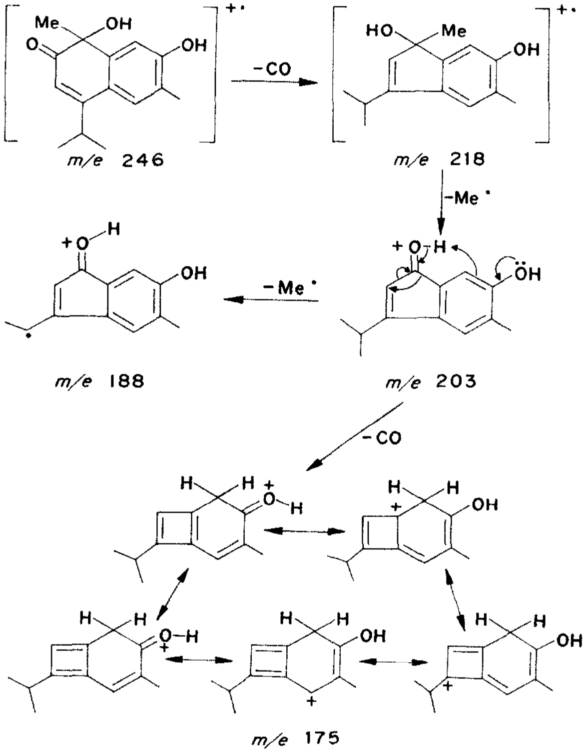


Fig. 1. Mass fragmentation of lacinilene C.

The high-resolution MS of the faster moving compound from cotton provided the formula $C_{16}H_{20}O_3$. The NMR spectrum was almost identical to that of lacinilene C, except for the appearance of an aromatic methoxy group at δ 3·82 (3H, *s*). The IR spectrum (CCl_4) provided evidence for a hydroxy group (3500 cm^{-1}) and a conjugated carbonyl group (1667 and 1605 cm^{-1}). The shift to higher wavenumbers [1645 cm^{-1} in **(3)** to 1667 cm^{-1} in **(4)**] is expected for conversion of a phenol to a methoxyl. As expected, the UV spectrum of **(4)** was unaltered on addition of base. The MS fragmentation pattern of the methyl ether **(4)** was also in good agreement with the parent phenol **(3)**. Thus both **(3)** and **(4)** readily lose CO, CO–Me, CO–2Me, and 2CO–Me; their base peaks differ in molecular weight by 14 amu. Acid hydrolysis of **(4)** produced lacinilene C **(3)** in low yield. Compound **(4)**, therefore, is the 7-methyl ether of lacinilene C.

EXPERIMENTAL

Extraction and isolation. Bracts from frost-killed, field-grown cotton (Paymaster 111 and 909), from Lubbock, Tex. were extracted with H_2O at room temp. H_2O extract was filtered and partitioned with Et_2O. Combined Et_2O portions were passed through anhydrous Na_2SO_4 and chromatographed on thin layers of Si gel (Et_2O). Two yellow fluorescent pigments were detected, eluted with Et_2O as one band, and rechromatographed on Si gel [$CHCl_3$–Me_2CO–HCO_2H (80:19:1)]. The slower-moving compound (lacinilene C) was then chromatographed with Et_2O–naphtha solvent (1:1) and $CHCl_3$–MeOH (95:5), and the faster-moving compound (lacinilene C7-methyl ether) was chromatographed with C_6H_6 and $CHCl_3$.

Lacinilene C, mp 57–60° (lit. 62–63° [3]); MS: *m/e* 246·125946 (30%) (calcd. for $C_{15}H_{18}O_3$: 246·125580), 218 (25%), 203 (53%), 188 (22%), 177 (27%), 176 (18%), 175 (100%), 161 (50%); IR: ν_{max}^{KBr} 3400, 1645, 1610, 1575, 1380, 1265, 1140 cm^{-1}; UV; λ_{max}^{EtOH} (ϵ) 227 (5800), 253 (5900), 290 (sh), 347 (2200), 370 (sh) nm; UV: $\lambda_{max}^{EtOH-NaOH}$ (ϵ) 246 (7400), 271 (4000), 314 (1700), 341 (1700), 443 (4800) nm.

Lacinilene C 7-methyl ether, yellow oil, MS: *m/e* 260·140899 (17%) (calcd. for $C_{16}H_{20}O_3$: 260·141230), 232 (28%), 217 (47%), 202 (14%), 190 (18%), 189 (100%), 187 (53%), 175 (38%); IR: $\nu_{max}^{CCl_4}$ 3500, 1667, 1605, 1460, 1380, 1320, 1275, 1190, 1175, 1140, 1045 cm^{-1}; UV: λ_{max}^{EtOH} (ϵ) 228 (7200), 250 (6500), 340 (2800), 370 (sh) nm; UV: $\lambda_{max}^{EtOH-NaOH}$ (ϵ) 249 (7200), 339 (4000) nm; NMR ($CDCl_3$): (δ) 1·24 (6H, *d* of *d*), 1·50 (3H, *s*), 2·18 (3H, *s*), 3·15 (1H, *m*), 3·82 (3H, *s*), 5·92 (1H, *s*), 7·10 (1H, *s*), 7·23 (1H, *s*).

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