REFERENCES

1 Hegnauer, R (1973) *Chemotaxonomie der Pflanzen* Band 6, pp 10–50 Birkhauser, Basel
2 Camps, P, Cardellach, J, Font, J, Ortuño, R M and Ponsati, O (1982) *Tetrahedron* **38**, 2395
3 Suga, T and Hirata, T (1982) *Bull Chem Soc Jpn* **55**, 1584
4 Tschesche, R, Wirth, W and Welmar, K (1981) *Phytochemistry* **20**, 1835
5 Tschesche, R, Welmar, K and Snatzke, G (1972) *Chem Ber* **105**, 290
6 Takahashi, K, Matsuzawa, S and Takani, M (1978) *Chem Pharm. Bull (Tokyo)* **26**, 1677
7 Westley, J W and Halpern, B (1968) *J Org Chem* **33**, 3978

Phytochemistry, Vol 23, No 10, pp 2396–2397, 1984
Printed in Great Britain

0031-9422/84 $3 00 + 0 00
Pergamon Press Ltd

1-(3,4-DIHYDROXY-5-METHOXYPHENYL)-3-METHYLBUT-2-ENE FROM THE LIVERWORT *PLAGIOCHILA RUTILANS*

SIEGFRIED HUNECK,* JOSEPH D CONNOLLY,† LESLIE J HARRISON,† ROBERT S I JOSEPH† and THOMAS POCS‡

*Institute of Plant Biochemistry, Research Centre for Molecular Biology and Medicine of the Academy of Sciences of the G D R, G D R -401 Halle/Saale, Weinberg, German Democratic Republic, † Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, U K, ‡ Research Institute for Botany of the Hungarian Academy of Sciences, 2163 Vácrátót, Hungary

(*Received* 24 *October* 1983)

Key Word Index—*Plagiochila rutilans*, Hepaticae, 1-(3,4-dihydroxy-5-methoxyphenyl)-3-methylbut-2-ene

Abstract—Extraction of the liverwort *Plagiochila rutilans* afforded 1-(3,4-dihydroxy-5-methoxyphenyl)-3-methylbut-2-ene, the structure of which was confirmed by synthesis

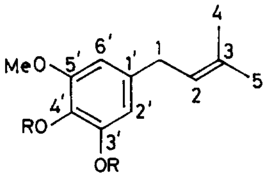
INTRODUCTION

The Cuban liverwort *Plagiochila rutilans* Lindb of the family Plagiochilaceae (Joerg) M Mull is characterized by its peppermint-like odour Chromatography of the diethyl ether extract of the liverwort, collected by one of us (T P) in Cuba, yielded, in addition to an oil with a peppermint-like odour, a crystalline compound which was shown to be 1-(3,4-dihydroxy-5-methoxyphenyl)-3-methylbut-2-ene (**1**) by an examination of its ^{1}H NMR and ^{13}C NMR spectra The structure was confirmed by synthesis

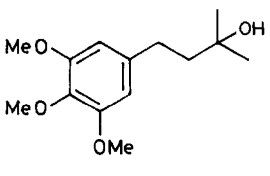
RESULTS AND DISCUSSION

Compound **1** had the formula $C_{12}H_{16}O_3$ (m/z 208) and resonances in its ^{1}H NMR spectrum for a dimethylallyl group attached to a benzene ring δ1 7 (*s*, 6H, 2 × vinyl Me), 3 2 (*d*, 2H, Ar–CH_2–) and 5 2 (*t*, 1H, –CH=C$<$) The trioxygenated nature of the aromatic ring was revealed by the presence of two *meta*-coupled aromatic protons [δ6 20 and 6 29 (both *d*, $J = 3$ Hz)], a methoxyl group (δ3 80) and two phenolic hydroxyl groups [δ4 7 (*br s*, 2H, exchangeable with D_2O)] The ^{13}C NMR chemical shifts of the oxygenated aromatic carbons (δ148 5, 137 2 and 146 9) clearly indicated that the oxygen functions were attached to positions C-3′, C-4′ and C-5′ while the non-equivalence of the *meta*-coupled aromatic protons required the attachment of the methoxyl group to positions C-3′ or C-5′ These data led uniquely to the structure 1-(3,4-dihydroxy-5-methoxyphenyl)-3-methylbut-2-ene (**1**) for the natural product

This structure was confirmed by synthesis Methyl 3-(3,4,5-trimethoxyphenyl)-propanoate [1], prepared by methylation and hydrogenation of 3,4,5-trimethoxycinnamic acid, was treated with excess methyl magnesium iodide to give the expected alcohol (**2**) Dehydration with



1 R = H
3 R = Me



2

thionyl chloride afforded a mixture of double-bond isomers [δ5 2 ($-\mathrm{CH}=\mathrm{C}<$), 4 75 ($-\mathrm{CH_2}-\mathrm{C}\lessgtr$)] in a ratio of 3 1 The desired isomer (3) was separated by preparative TLC on silver nitrate-impregnated silica gel plates Partial demethylation of 3 was achieved by use of lithium aluminium hydride in benzene [2] This reaction is critically dependent on the condition of the lithium aluminium hydride which must be quite fresh The product was obtained as a pale yellow solid of mp 94–95°, identical in all respects to the natural product

The chemical constituents of bryophytes form the subject of recent reviews by Asakawa [3] and Huneck [4] The simple aromatic compounds reported so far include *p*-ethylanisole from *Leptolejeunea elliptica* [3, 4], 1-vinyl-3,4-dimethoxybenzene from *Conocephalum conicum* [3, 4] and *Marchesinia brachiata* [5], eugenol from *Anthelia julacea*, *Frullania jackii* and *Marchesinia mackaii* [3, 4], *o*- and *p*-hydroxybenzoic acids and *m*- and *p*-coumaric acids from *Sphagnum cuspidatum* and *S palustre* [4], methyl *p*-coumarate and methyl caffeate from *Anthoceros laevis* and *A punctatus* [3, 4], and 1-allyl-3,5-dimethoxy-4-hydroxybenzene from *Marchesinia brachiata* [5] *Plagiochila* species have been found to contain a variety of sesquiterpenoids, in particular *ent*-2,3-secoaromadendranes, bibenzyls and flavonoids [3, 4]

EXPERIMENTAL

Extraction of Plagiochila rutilans The air-dried and powdered liverwort (11 g, from Cuba, Gran Piedra rocks, leg T Pócs, det H Inoue, voucher specimen deposited at the herbaria of T P and S H) was extracted with $\mathrm{Et_2O}$ for 16 hr Removal of the solvent afforded an oily residue which was chromatographed on silica gel in *n*-hexane with increasing amounts of $\mathrm{Et_2O}$ The early fractions contained an oil with a strong peppermint odour These were followed by a crystalline fraction which, on recrystallization from $\mathrm{Et_2O}$–*n*-hexane yielded 1-(3,4-dihydroxy-5-methoxyphenyl)-3-methylbut-2-ene (1) (17 5 mg, 0 15 %) as needles of mp 94–95° IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1} 796, 820, 840, 876, 944, 990, 1080, 1142, 1186, 1218, 1332, 1370, 1440, 1468, 1500, 1600, 1618, 2960, 3500 UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε) 207, (4 10), 291 (3 30), $\lambda_{\max}^{\mathrm{MeOH+NaOH}}$ nm (log ε) 207 (4 11), 265 (3 76) MS *m/z* (rel int) 208 $[\mathrm{M}]^+$ (100), 193 $[\mathrm{M}-\mathrm{Me}]^+$ (16), 153 (80), 152 $[\mathrm{M}-\mathrm{C_4H_8}]^+$ (98), 125 (54), 124 $[\mathrm{M}-\mathrm{C_4H_8}-\mathrm{CO}]^+$ (46), 123 (54), 109 $[\mathrm{M}-\mathrm{C_4H_8}-\mathrm{CO}-\mathrm{Me}]^+$ (34) ^{13}C NMR δ127 9 (C-1′), 97 4 (C-2′), 148 5 and 146 9 (C-3′ and C-5′), 137 2 (C-4′), 107 7 (C-6′), 28 0 (C-1), 122 0 (C-2), 133 0 (C-3), 17 8 (C-4), 25 8 (C-5), 56 0 (OMe)

Synthesis of compound 1 3,4,5-Trimethoxycinnamic acid (1 1 g) in MeOH was treated with excess $\mathrm{CH_2N_2}$ Crystallization from EtOAc–*n*-hexane gave the methyl ester (1 02 g), mp 99–100°, *m/z* 252 ($[\mathrm{M}]^+$), which was hydrogenated over Pd/C in EtOAc under normal conditions The product, the dihydro-methyl ester (0 98 g) [δ2 8 (4 H, *m*, $-\mathrm{CH_2}-\mathrm{CH_2}-$)] was a yellow oil Reaction with MeMgI in $\mathrm{Et_2O}$ under standard conditions afforded a red-brown oil (0 91 g) which showed several spots in TLC The major component, the alcohol 2 (514 mg), was isolated as a colourless, viscous oil, *m/z* 254 $[\mathrm{M}]^+$ ^{1}H NMR δ6 42 (2 H, *s*, H-2′ and H-6′), 3 84 (9H, 3 × OMe), 2 63 (2H, *t*, J = 7 Hz, H-1), 1 75 (2H, *t*, J = 7 Hz, H-2), 1 27 (6H, 2 × Me) ^{13}C NMR δ136 2 (C-1′), 105 4 (C-2′ and C-6′), 153 2 (C-3′ and C-5′), 138 4 (C-4′), 31 2 (C-1), 45 7 (C-2), 70 3 (C-3), 29 4 (C-4 and C-5), 56 1 (OMe)

Alcohol 2 (574 mg) in dry, redistilled pyridine at 0° was treated with excess redistilled $\mathrm{SOCl_2}$ After 5 min cold aq $\mathrm{NaHCO_3}$ soln was added and the mixture extracted with $\mathrm{CHCl_3}$ Prep TLC of a portion (165 mg) of the brown, viscous, oily product gave the major component as a yellow, viscous oil (93 mg) whose ^{1}H NMR spectrum showed it to be a mixture of double-bond isomers Preparative TLC on $\mathrm{AgNO_3}$-impregnated silica gel plates in the dark afforded the dimethylallyl isomer (3) as a yellow oil (30 mg)

Alkene 3 (30 mg) in dry $\mathrm{C_6H_6}$ (20 ml) was refluxed with fresh $\mathrm{LiAlH_4}$ (9 mg) for 12 hr Work-up by addition of wet $\mathrm{Et_2O}$, dil HCl and EtOAc and removal of the solvent yielded a yellow, viscous oil which showed a major spot on TLC Purification by prep TLC gave 1-(3,4-dihydroxy-5-methoxyphenyl)-3-methylbut-2-ene (1) as a pale yellow solid, identical (^{1}H NMR, MS, TLC) to the natural product

REFERENCES

1 Kato, M , Kido, F , Wu, M -D and Yoshikoshi, A (1974) *Bull Chem Soc Jpn* **47**, 1516

2 Carroll, J F , Kulkowit, S and McKervey, M A (1980) *J Chem Soc Chem Commun* 507

3 Asakawa, Y (1982) *Prog Chem Org Nat Prod* **42**, 1

4 Huneck, S (1983) in *New Manual of Bryology*, Vol 1 J Hattori Bot Lab , Tokyo

5 Gradstein, S R , Matsuda, R and Asakawa, Y (1981) *J Hattori Bot Lab* **50**, 231