

2-*O*-Methylobtusatic Acid, a New Depside from the Lichen *Xanthoparmelia tusconensis*

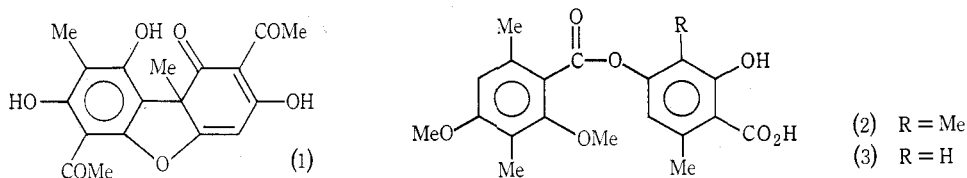
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Abstract

The depside, 2-*O*-methylobtusatic acid [4-(2',4'-dimethoxy-3',6'-dimethylbenzoyloxy)-2-hydroxy-6-methylbenzoic acid]* has been prepared by unambiguous synthesis and shown to co-occur with usnic acid and diffractaic acid in the lichen *Xanthoparmelia tusconensis*.

In the course of our chemotaxonomic survey of the lichens of eastern Australia^{1,2} we made comparisons with a number of the North American species. One such specimen, the lichen *Xanthoparmelia tusconensis* (Nash) Egan, was found to produce three major phenolic metabolites, only two of which correspond to known lichen substances.



Usnic acid (1) and diffractaic acid (2) were readily identified as components of the lichen by comparison with authentic materials. Subsequently we have undertaken the synthesis of 2-*O*-methylobtusatic acid (3). The thin-layer chromatographic behaviour of the latter compound in three independent solvent systems³ was identical to that of the unknown lichen depside present in *X. tusconensis*.

Synthesis of the Depside

The preparation of the carboxylic acid, 2,4-dimethoxy-3,6-dimethylbenzoic acid (4), and the phenolic ester, benzyl orsellinate (5), has been described previously.⁴

Depside ester formation between (4) and (5) was achieved by treatment with trifluoroacetic anhydride and yielded benzyl 2-*O*-methylobtusate (6). Catalytic hydrogenolysis of the benzyl ester (6) proceeded to give 2-*O*-methylobtusatic acid (3).

* Note that in systematic nomenclature, as distinct from trivial nomenclature, the ring carbons of the benzoic acid moiety are unprimed and those of the benzoyloxy moiety primed.

¹ Elix, J. A., *Aust. J. Chem.*, 1975, **28**, 849.

² Elix, J. A., and Tearne, P. D., *Aust. J. Chem.*, 1977, **30**, 2333, and references therein.

³ Culberson, C. F., *J. Chromatogr.*, 1972, **72**, 113.

⁴ Elix, J. A., and Norfolk, S., *Aust. J. Chem.*, 1975, **28**, 1113.

in good yield. The ^1H n.m.r. and mass spectral data recorded for the new depside were consistent with those observed previously for related *para*- β -orcinol depsides.⁴

As thin-layer chromatography is now undoubtedly the most widely used method for the identification of lichen constituents,³ the relevant data for 2-*O*-methylobtusatic acid (3) are listed in Table 1.

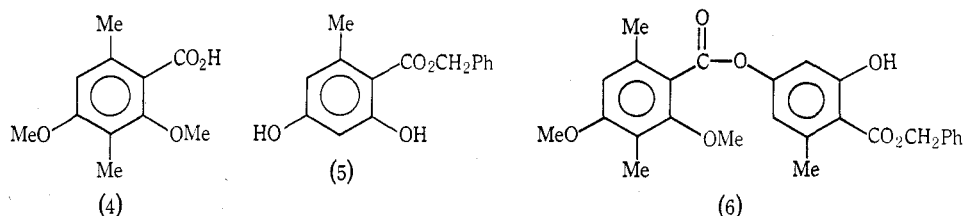


Table 1. T.l.c. data for 2-*O*-methylobtusatic acid

On silica gel; A, benzene/dioxan/acetic acid 180/45/5; B, n-hexane/diethyl ether/formic acid 130/80/20; C, toluene/acetic acid 200/30

Compound	R_F (A)	R_F (B)	R_F (C)
Usnic acid (internal standard)	0.71	0.70	0.70
Diffraitaic acid (internal standard)	0.45	0.64	0.51
2- <i>O</i> -Methylobtusatic acid: synthetic	0.42	0.56	0.46
in <i>X. tusconensis</i>	0.42	0.57	0.46

Experimental

The general experimental details have been published previously.⁵

Benzyl 2-*O*-Methylobtusate (6)

A mixture of 2,4-dimethoxy-3,6-dimethylbenzoic acid (4) (1 mmol) and benzyl orsellinate (5) (1 mmol) was dissolved in a solution of anhydrous toluene (4 ml) and trifluoroacetic anhydride (1 ml) and permitted to stand at room temperature for 2 h. The solvent was then removed under reduced pressure and the residue adsorbed on a thick-layer plate. Elution with 20% ethyl acetate/light petroleum developed one major band, *benzyl 2-O-methylobtusate* (6) (0.25 g, 56%) as a colourless oil. ^1H n.m.r. δ (CDCl_3) 2.15, 2.44, 2.53, each s, ArCH_3 ; 3.84, s, $2 \times \text{OCH}_3$; 5.42, s, OCH_2 ; 6.52, s, ArH ; 6.66, 6.81, each d, J 2 Hz, ArH ; 7.38, s, $\text{OCH}_2\text{C}_6\text{H}_5$; 11.64, s, OH.

2-*O*-Methylobtusatic Acid (3)

The depside ester (6) (0.5 mmol) was dissolved in ethyl acetate (5 ml) containing 10% palladium-on-carbon (25 mg), and the suspension was stirred in an atmosphere of hydrogen for 2 h. The catalyst was then filtered and the solvent evaporated. 2-*O*-Methylobtusatic acid (3) (0.15 g, 84%) was recrystallized from toluene/acetone as colourless crystals, m.p. 174° (Found: C, 63.7; H, 5.9. $\text{C}_{19}\text{H}_{20}\text{O}_7$ requires C, 63.3; H, 5.6%). ^1H n.m.r. δ (CD_3COCD_3) 2.14, 2.45, 2.68, each s, ArCH_3 ; 3.87, 3.93, each s, OCH_3 ; 6.79, s, $3 \times \text{ArH}$. Mass spectrum m/e 360 (M , $<1\%$), 193 (100), 150 (8).

Acknowledgment

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⁵ Elix, J. A., *Aust. J. Chem.*, 1974, **27**, 1767.