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STRUCTURE OF POROSIN*

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Key Word Index—*Ocotea porosa*; Lauraceae; porosin; neolignan; photodegradation of porosin; *rel*-(2S,3R,3aS,5S)-3a-allyl-5-methoxy-3-methyl-2-veratryl-2,3,3a,4,5,6-hexahydro-6-oxobenzofuran.

Abstract—The reported structure of porosin, 3a-allyl-5-methoxy-3-methyl-2-veratryl-2,3,3a,6,7,7a-hexahydro-6-oxobenzofuran, is revised with respect to Δ-4,5. ^{1}H NMR (LIS), UV and photochemical evidence shows that the double bond is located at the 7,7a-position.

The structural proposal **1** for porosin was based on ^{1}H NMR and MS evidence, obtained for this neolignan of *Ocotea porosa* (Nees) L. Barr. (Lauraceae) and for its two hexahydro-derivatives [2]. Structure **2** was not considered, in view of the probable biosynthetic reaction sequence (which includes step **3** → **1**) [3] and the closeness of the ^{1}H NMR frequencies of the aliphatic methoxyls in porosin (δ 3.62) and in burchellin (**4**, δ 3.68) [4,5,6], both of which seem to require location of the OMe groups at sp^2-C. Clearly, however, a change in the direction of enolization (**3** → **5**) is mechanistically defendable as one of the later steps in the biosynthesis of porosin (which would then be concluded by **5** → **2**). Furthermore, all ^{1}H NMR data are equally interpretable on grounds of structure **2** in which the oxymethine hydrogen, assigned to C-7a in **1**, occupies C-5. Since this shows axial-axial interaction with a vicinal proton, the pseudoequatorial OMe at C-5 must be situated near the plane of the carbonyl, a fact which may explain the appearance of the corresponding ^{1}H NMR singlet at lower field than expected for a methoxyl on sp^3-C.

The preceding re-evaluation of data became necessary when the Pr(FOD)$_3$ ^{1}H NMR shifts for some neolignans were considered (Table). These are relatively feeble in the case of porosin, and, thus, incompatible with the existence of the planar CH=C.OMe.C=O system shown in **1**.

Further evidence for the validity of structure **2** for porosin was based on the evaluation of the chromophores of **1** and **2**, first by direct and subsequently also by indirect UV evidence. Initially, after spectra of model compounds had been obtained (Fig. 1), the addition curve for **6** and **7** [7], and not **6** and **8** [8], proved to be close to the spectrum of porosin (Fig. 2). The indirect method relied on the argument that elimination of the C-5 methoxyl from a double bond of an α,β-unsaturated carbonyl

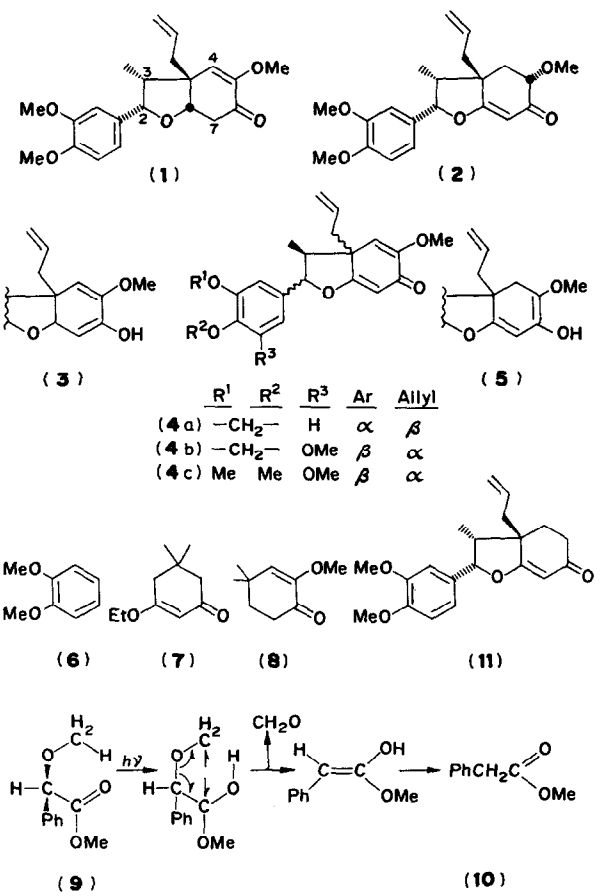

Table 1. Pr(FOD)$_3$ induced shifts (Δδ) obtained by extrapolation of observed shifts (in $CDCl_3$) to 1:1 shift reagent–substrate mole ratio

	(4a) [5]	(4b) [5]	(4c) [5]	Porosin (2)
H-4	11.7	11.4	11.5	ax. 1.4; eq. 4.3
OMe-5	27.0	23.0	24.8	13.4
H-7	9.1	9.5	9.3	2.4

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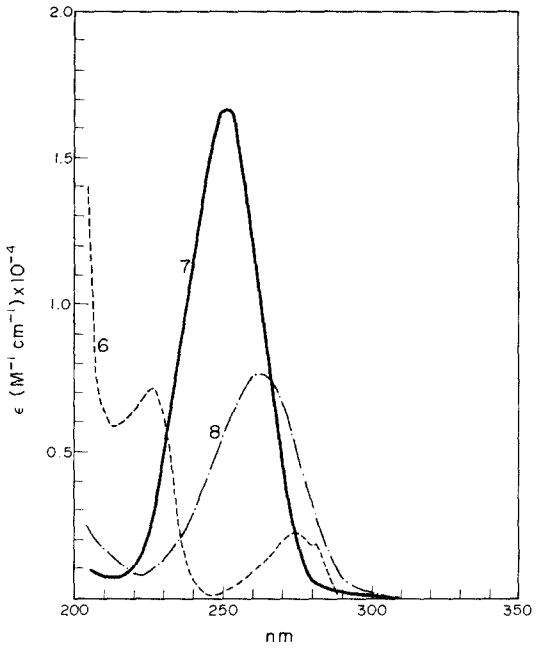

Fig. 1. UV spectra of compounds **6**, **7** and **8** in MeOH.

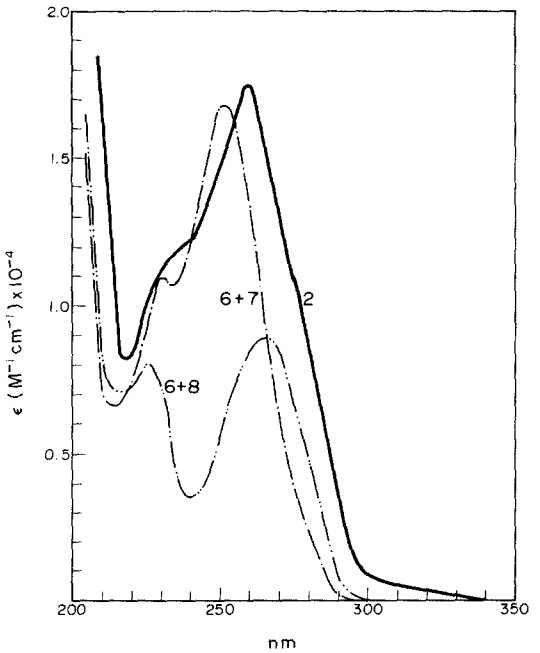

Fig. 2. UV spectrum of porosin (**2**) in MeOH. Addition curves of UV spectra of compounds **6**, **7** and **6**, **8**.

system (such as in **1**) would modify the UV absorption, while removal of the methoxyl from a saturated C should not modify the chromophore of **2**.

Photolytic removal of the methoxyl at the asymmetric center of methyl (+)-O-methylmandelate (**9**→**10**) proceeds in good yield [9] and provides a model for the required reaction, since **2**, if envisaged as the vinylogue of an α-methoxyester, possesses analogous functionality. Indeed, irradiation at 254 nm of porosin in methanol gave, in a reaction to be described in detail in a forthcoming paper, a demethoxy-derivative (**11**) in over 50% yield. Comparison of the ^{1}H NMR spectra of porosin and **11** left no doubt that the reaction had occurred in the expected direction. In **11**, a double bond sustaining a lone olefinic proton can, of course, be placed only between 7 and 7a. The invariance of the frequency of the corresponding ^{1}H-signal (in $CDCl_3$) for porosin (δ 5.59) and the reaction product (δ 5.56) is evidence that the enone systems are seated in identical surroundings, corroborating structure **2** for porosin. Thus, the UV spectra of porosin (**2**) and the photodecomposition product **11** should be superimposable, and this is indeed the case.

Structure **2** for porosin was confirmed by ^{13}C NMR [10].

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