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EPOXYCONIFERYL ALCOHOL FROM *FRAXINUS OXYCARPA* BARK

IVANKA KOSTOVA,* DRAGOMIR DINCHEV, BOZHANA MIKHOVA and TANYA IOSSIFOVA

Institute of Organic Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

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Key Word Index—*Fraxinus oxycarpa*; Oleaceae; bark; hydroxycoumarins; secoiridoids; phenolic compounds; epoxyconiferyl alcohol.

Abstract—The new compound, epoxyconiferyl alcohol, has been isolated from the bark of *Fraxinus oxycarpa*, along with the known hydroxycoumarins, esculin, fraxin, esculetin, isoscopoletin, fraxetin, and the secoiridoids, ligstroside and 10-hydroxyligstroside.

INTRODUCTION

In continuation of our phytochemical investigations on *Fraxinus* species [1, 2], we examined the bark of *F. oxycarpa* Willd., growing in Bulgaria. Previous works on this plant describe the presence of some phenolic acids and the hydroxycoumarins esculetin, isofraxinol, esculin, fraxin and cichoriin [3, 4]. The present study has resulted in the isolation of a new phenolic compound epoxyconiferyl alcohol (**1**) and seven known substances. This report deals with the isolation and structural elucidation of the new compound.

RESULTS AND DISCUSSION

The DXE and ethanol extracts of the bark of *F. oxycarpa* were fractionated and worked-up as described in the Experimental, to give epoxyconiferyl alcohol (**1**), together with the coumarins esculin, fraxin, esculetin, fraxetin and isoscopoletin, as well as the secoiridoid glucosides, ligstroside and 10-hydroxyligstroside. This is the first report of the occurrence of the last five compounds in *F. oxycarpa*.

Epoxyconiferyl alcohol (**1**), $C_{10}H_8O_4$, was obtained as an amorphous powder. It showed UV maxima at 281 nm in ethanol and IR bands at 1237, 823 and 752 cm^{-1}. Its ^1H NMR spectrum (Table 1) revealed the typical pattern of a 1,3,4-trisubstituted benzene ring at δ6.90 (*d*, J = 1.7 Hz), 6.89 (*d*, J = 8.2 Hz) and 6.82 (*dd*, J = 1.7 and 8.2 Hz), one aromatic OMe at δ3.91 (*s*, 3H) and one phenolic OH at δ5.59 (*bs*, D_2O-exchangeable). Oxirane protons appeared as a multiplet at δ3.10 (H-2′) and a doublet at δ4.74 (J = 4.2 Hz, H-3′). The observed coupling constant of 4.2 Hz suggested a *cis*-disubstituted epoxide [5]. ^1H decoupling showed that the remaining two signals (*dd*) at δ3.88 and 4.25 belong to a methylene group attached to C-2′. The position of the substituents in the aromatic ring and the *cis*-configuration of the oxirane protons were confirmed by NOE experiments (Fig. 1).

The ^{13}C NMR data (Table 1) were in agreement with the structure of **1** as epoxyconiferyl alcohol.

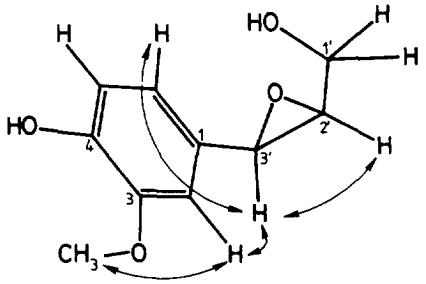


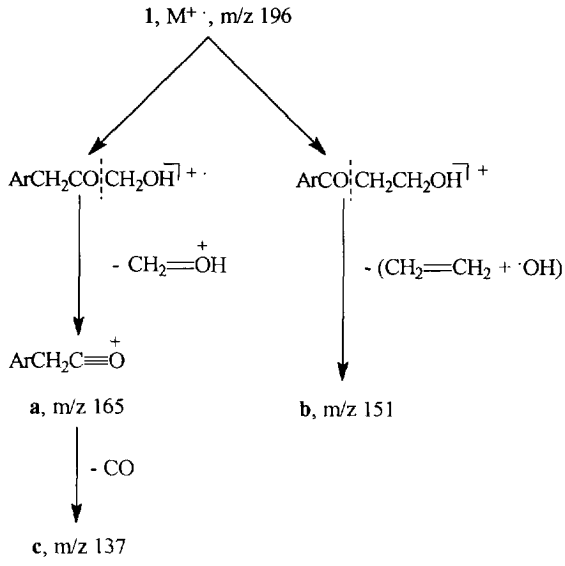
Fig. 1. Most important enhancements of signals in homonuclear ^1H NOE spectra of **1**. Arrows (↷) designate mutual effect between the indicated protons.

Table 1. ^1H and ^{13}C NMR spectral data of epoxyconiferyl alcohol (**1**) in $CDCl_3$

Position	δH (J in Hz)	δC
1	—	133.0 *s*
2	6.90 *d* (1.7)	108.6 *d*
3	—	146.7 *s*
4	5.59 *bs* (OH, D_2O-exchangeable)	145.3 *s*
5	6.89 *d* (8.2)	114.3 *d*
6	6.82 *dd* (8.2, 1.7)	119.0 *d*
1′	3.88 *dd* (9.0, 3.7)	71.7 *t*
	4.25 *dd* (9.0, 7.0)	
2′	3.10 *m*	54.2 *d*
3′	4.74 *d* (4.2)	85.9 *d*
OMe	3.91 *s*	56.0 *q*

*Author to whom correspondence should be addressed.

The mass spectral behaviour of **1** provided further evidence for the proposed structure. The 70 eV mass spectrum exhibited a $[M]^+$ at *m/z* 196 and the presence of characteristic ions a (*m/z* 165), b (*m/z* 151) and c (*m/z* 137). These ions could be attributed to the specific rearrangement of the epoxy ring [6] with formation of the corresponding carbonyl compounds of the type $ArCH_2COCH_2OH$ and $ArCOCH_2CH_2OH$, followed by cleavage α to the carbonyl group (Scheme 1).



Scheme 1. Mass spectral cleavage of **1**.

EXPERIMENTAL

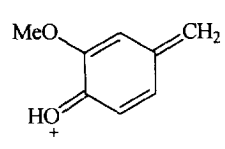
General. ^1H and ^{13}C NMR spectra [δ(ppm), J(Hz)] were obtained at 250 and 63 MHz, respectively, using TMS as int. standard. NOE experiments were performed using standard Bruker software. MS: 70 eV. TLC: aluminium sheets, silica gel 60 F_{254} (Merck), bands detected under UV light, after exposure to I_2 vapour or by spraying with H_2SO_4 and heating. Prep. TLC: 20 × 20 cm plates coated with 1 mm of silica gel PF_{254} (Merck), bands detected in UV light and after exposure to I_2 vapour. Liquid vacuum chromatography (LVC): silica gel LS 5–40 μ (Chemapol). TLC solvent systems: Et_2O–toluene (2:1), satd with 10% HOAc (A), Et_2O–toluene–EtOAc (2:1:1) (**B**), Et_2O–toluene–EtOAc (9:4:3) (C) and MeOH–$CHCl_3$–HCO_2H (5:0.8:0.2) (D).

Plant material. A sample of *F. oxycarpa* Willd. bark, collected in 1990 from the region of Kresna, South Bulgaria, was studied. A voucher specimen is deposited in the herbarium of the Institute of Botany, BAS, Sofia.

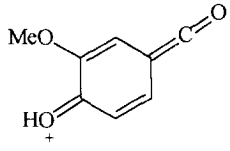
Isolation of compounds. Dried and well-ground bark (1.6 kg) was successively extracted with petrol (3 × 3 l), DXE (3 × 2.2 l) and EtOH (3 × 2 l) at room temp.

The DXE extract (8.2 g) was subjected to LVC over 80 g silica gel (petrol–$CHCl_3$, 1:1, 1:2 and 1:3). The frs. eluted with petrol–$CHCl_3$ (1:2) and (1:3) on concn under red. pres. afforded residues R-1 (0.25 g) and R-2 (0.10 g), respectively. R-1 was chromatographed on a silica gel column with petrol–$CHCl_3$ mixts of increasing polarity. The frs obtained with petrol–$CHCl_3$ (1.5:1) were subjected to prep. TLC (C, multiple development) to give **1** (0.01 g). Prep. TLC (C) of 0.02 g of R-1 gave isoscopoletin (0.003 g). Prep. TLC of R-2 in the same solvent system yielded esculetin (0.003 g) and fraxetin (0.005 g)..

A part of the EtOH extract (5.8 g) was subjected to LVC over 70 g silica gel using DXE–MeOH mixts of increasing polarity (30:1, 8:1 and 5:1). Frs eluted with DXE-MeOH (8:1) and DXE–MeOH (5:1) on concn gave residues R-3 (0.65 g) and R-4 (0.27 g). R-3 on CC over silica gel and elution with $CHCl_3$–MeOH (8:1) afforded pure ligstroside (0.094 g). R-4 on CC over silica gel and prep. TLC (D) of the frs eluted with $CHCl_3$–MeOH (5:1) gave esculin (0.005 g) and fraxin (0.005 g).



c, m/z 137



b, m/z 151

Epoxyconiferyl alcohol (**1**). Powder. $[\alpha]_D^{20}$ + 51.56° ($CHCl_3$; *c* 0.4325). UV λ_{max}^{EtOH} nm (log ε): 281 (3.46). IR ν_{max}^{KBr} cm^{-1}: 3420, 3007, 1604, 1517, 1450, 1237, 823, 752. EIMS *m/z* (rel. int.): 196 $[M]^+$ (8), 165 (a, 8), 151 (b, 100), 137 (c, 38). ^1H and ^{13}C NMR: Table 1.

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REFERENCES

1. Kostova, I. (1992) *Planta Med.* **58**, 484.
2. Iossifova, T., Mikhova, B. and Kostova, I. (1993) *Phytochemistry* **34**, 1373.
3. Artemeva, M. V., Karryev, M. O. and Nikonov, G. K. (1979) *Rastit. Resur.* **11**, 368.
4. Grujic-Vasic, J. and Ramic, S. (1968) *Lek. Sirovine* **6**, 25.
5. Aycard, J., Kini, F., Kam, B., Gaydou, E. and Faure, R. (1993) *J. Nat. Prod.* **56**, 1171.
6. Porter, Q. N. and Baldas, J. (1971) in *Mass Spectrometry of Heterocyclic Compounds* (Weissberger. A. and Taylor, E. G., eds), pp. 18–19. Wiley-Interscience, New York.