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COMPOSITAE

QUERCETIN 3-β-GLUCOSIDE FROM *AMBROSIA TRIFIDA*

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Plant. Ambrosia trifida.

Flowers. Quercetin 3-glucoside (identified by m.p., u.v., NMR and chromatographic comparison with authentic specimen).

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FAGACEAE

BRANCHED NONALACTONES FROM SOME *QUERCUS* SPECIES

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Abstract—Two diastereomers of 3-methyl-4-hydroxy caprylic acid γ-lactone were isolated from the wood of three *Quercus* species.

TWO DIASTEREOMERS of a branched nonalactone were isolated together with γ-nonalactone and eugenol from the woods of *Quercus mongolica* Fisch. var *grosseserrata* Rehd. et Wils., *Q. serrata* Thunb. and a white oak* (Fagaceae).

Both compounds, which we named *Quercus* lactones-a and -b, exhibited almost the same i.r. spectra with absorption at 1770 cm^{-1} indicating their γ-lactonic function. The mass spectra showed parent peaks at *m/e* 156 and base peaks at *m/e* 99. The NMR spectrum (in $CDCl_3$) disclosed signals at δ 0·92 (3H, s, $\mathrm{C\underline{H}_3}$—), 1·11 (3H, d, $J = 6$ Hz, $\mathrm{C\underline{H}_3}$—CH—), and 3·88 (1H, m, =C$\underline{\mathrm{H}}$—O—CO—) for *Quercus* lactone-a and at δ 0·92 (3H, s, $\mathrm{C\underline{H}_3}$—), 1·00 (3H, d, $J = 7$ Hz, $\mathrm{C\underline{H}_3}$—CH—), and 4·37 (1H, m, =C$\underline{\mathrm{H}}$—O—CO—) for *Quercus* lactone-b. These spectral data suggest that both compounds have structure (I).

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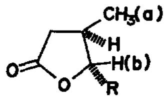
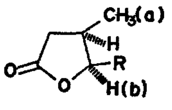
* 'White oak' is a general name for the group of deciduous oaks grown in North America and could refer to *Q. alba*, *Q macrocarpa*, *Q. montana*, *Q. muehlenbergii*, *Q. virginiana*, *Q. lylata*, *Q. stellata* or *Q. prinus*.



trans



cis

(IIa) *trans*, (IIb) *cis*: $R = CH_3$
(Ia) *trans*, (Ib) *cis*: $R = (CH_2)_3CH_3$

Reformatosky reaction between ethyl bromacetate and heptan-2-one followed by dehydration and cyclization with conc. H_2SO_4 gave *Quercus* lactones-a and -b together, indicating that the compounds are diastereoisomers of (I).

Laporte[1] studied the NMR spectra of two isomers of 3-methyl-4-hydroxyvaleric acid γ-lactone (IIa and IIb) and assigned signals for the methyl and methine protons as shown in the following table.

TABLE 1

		a (ppm)	b (ppm)
IIa	*trans*	1·25	4·60
IIb	*cis*	1·35	4 05
I	lactone-b	1 00	4 37
	lactone-a	1 11	3 88

From this it can be concluded that *Quercus* lactone-a is the *cis* (Ia) and *Quercus* lactone-b is the *trans* isomer (Ib).

A survey showed that these lactones were absent from evergreen oaks such as *Q. glauca* Thunb. and *Q. phillyraeoides* A. Grey.

The woods of white oak group and some other oaks are widely used for making barrels for aging spirits such as whisky and brandy, and it is interesting that these lactones were detected as ingredients of aged whiskies by Suomalainen[2] and us[3] independently.

EXPERIMENTAL

Isolation of Lactones

The shavings of the woods were extracted with methanol for a week. The extracts were steam distilled to obtain the volatile compounds. The volatiles were separated by means of silica-gel column to give lactone fraction For final isolation of lactones, preparative GLC with the column of Carbowax 20M was adopted. Optical rotations of the pure lactones were: lactone-a $[\alpha]_D^{26} + 62·5°$; lactone-b $[\alpha]_D^{26} - 6·9°$.

Synthesis

Quercus lactones-a and -b were prepared by treatment of ethyl bromacetate and heptan-2-one followed by dehydration and cyclization with conc H_2SO_4 after the method of Obata[4] The reaction mixture was subjected to chromatography on silica-gel to afford two fractions which both gave single peaks on gas chromatogram using a 45 m × 0·25 mm I D. capillary column coated with Ucon oil HB-2000, respectively.

The compound of the first fraction corresponded to *Quercus* lactone-a and that of the second fraction to *Quercus* lactone-b in their retention times of GLC and in their i.r., NMR and m.s. spectra.

Acknowledgement—The authors thank Dr. Y. Hirose, the Institute of Food Chemistry, for his kind advice.

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[1] J. F. LAPORTE, *Compt Rend., Ser.* C **262**, 1095 (1966).

[2] H. SUOMALAINEN and L. NYKÄNEN, *Naeringsmiddelindustrien*, No. 1/2, 1 (1970).

[3] M. MASUDA and K. NISHIMURA, unpublished data.

[4] S. OBATA, *Pharm Bull Japan* **73**, 1295 (1953)