

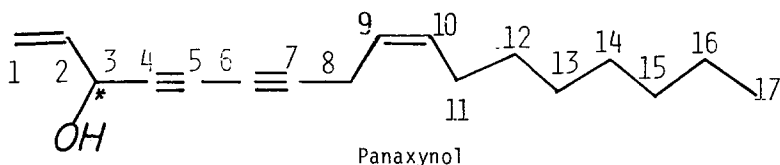
DETERMINATION OF ABSOLUTE STEREOCHEMISTRY OF PANAXYNOL

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Abstract: Absolute stereochemistry of panaxynol was determined by exciton chirality method. The circular dichroism spectra of panaxynol *p*-bromobenzoate and *p*-dimethylaminobenzoate show the negative exciton chirality at λ_{ext} indicating the *S* configuration of the chiral center.

Some naturally occurring poly-yne compounds have been isolated from Araliaceae plant family including the most important medicinal plant Panax ginseng C. A. Meyer.¹ Panaxynol which is a C₁₇ poly-yne compound isolated from ginseng roots has the chemical structure identical with falcarinol isolated from Falcaria vulgaris B.² and Carotatoxin isolated from Daucus carota L.³ However, absolute configuration of this poly-yne compound has not been studied due to its unstability even though it is very important in the view of its biological activity.



This panaxynol possesses the secondary allylic alcohol group at 3 position which has the chirality. In order to study the absolute configuration of this chiral center where the conformations are dynamic, a circular dichroic exciton chirality method was applied to two *p*-substituted benzoate derivatives of panaxynol.

The circular dichroic exciton method,^{4,6} a nonempirical method based on the coupled oscillator theory, has been applied to various organic compounds for the configurational studies. Recently, it is reported that the exciton chirality is constituted by the interaction between the *p*-substituted benzoate and double bond chromophores.⁵

Panaxynol from Korean ginseng roots is isolated by the method previously reported.⁷ The panaxynol benzoate derivatives prepared by the reaction of panaxynol with *p*-bromobenzoic acid and *p*-dimethylaminobenzoic acid under the reaction system of dicyclohexylcarbodiimide and 4-(dimethylamino)pyridine as a catalyst. These panaxynol benzoate derivatives were separated by low pressure preparative liquid chromatography.

The UV spectrum taken in methanol and other spectral data indicate that secondary allylic

alcohol is transformed into *p*-substituted benzoates.

Figure 1 show the circular dichroism spectra of panaxynol *p*-bromobenzoate and *p*-dimethylaminobenzoate. The ellipticity obtained from the circular dichroism spectra was transformed into molar circular dichroism. If two long axes of benzoate and double bond chromophore constitute a positive exciton chirality, that is right handed screwness, the Cotton effect at 1L_a band is positive. On the other hand, if allylic benzoate constitutes a negative exciton chirality, 1L_a benzoate Cotton effect should be negative. The value of molar circular dichroism for *p*-bromobenzoate and *p*-dimethylaminobenzoate are -4.76 at 244_{ext} and -4.45 at 313_{ext} respectively. From the observation that the values of molar circular dichroism of two benzoates are negative, it is concluded that the secondary allylic benzoates constitute negative exciton chirality indicating the *S* configuration of the chiral center in panaxynol.

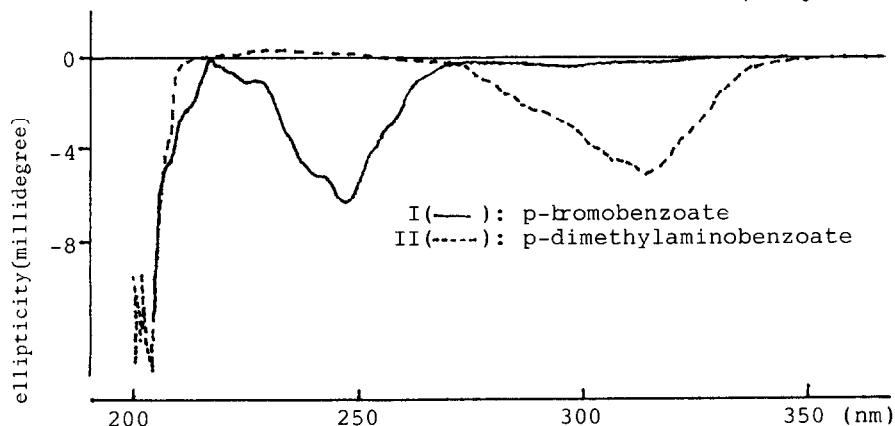


Figure 1. Circular Dichroism Spectra of *p*-Substituted Benzoates of Panaxynol

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Footnotes and References

1. F. Bohlmann, T. Burkhart and C. Zero, in "Naturally Occurring Acetylenes", Academic Press, London and New York, 1973
2. F. Bohlmann, U. Niedballa and K.-M. Rode, *Chem. Ber.*, **99**, 3552 (1966).
3. D.G. Crosby and N. Aharonson, *Tetrahedron*, **23**, 465 (1967).
4. N. Harada, K. Nakanishi, *Acc. Chem. Res.*, **5**, 257 (1972).
5. N.C. Gonnella, K. Nakanishi, V.S. Martin and K.B. Sharpless, *J. Amer. Chem. Soc.*, **104**, 3775 (1982).
6. N. Harada, H. Uda, *J. Amer. Chem. Soc.*, **100**, 8022 (1978).
7. S.C. Shim, H.Y. Koh and B.H. Han, *Phytochem.*, **22**, 1817 (1983).
8. a) *p*-bromobenzoate: UV (MeOH), $\lambda_{\text{max}} = 244$ nm; IR (NaCl), 2250 cm^{-1} ($\nu_{\text{C}=\text{C}}$) and 1730 cm^{-1} ($\nu_{\text{C}=\text{O}}$); $^1\text{H NMR}$ (80MHz, CDCl_3), $\delta = 7.51\text{--}7.97$ (m, 4H; C_6H_4), 6.15 (d, 1H; CH-U), 5.42 (m, 2H; CH=CH), 5.32-6.00 (m, 3H; $\text{CH}_2=\text{CH-}$), 3.06 (d, 2H; CH_2), 1.85-2.20 (br.m, 2H; CH_2), 1.30 (br.s, 10H; CH_2), 0.90 (br.t, 3H; CH_3).
- b) *p*-dimethylaminobenzoate: UV (MeOH), $\lambda_{\text{max}} = 313$ nm; IR (NaCl), 2250 cm^{-1} ($\nu_{\text{C}=\text{C}}$) and 1730 cm^{-1} ($\nu_{\text{C}=\text{O}}$); $^1\text{H NMR}$ (80MHz, CDCl_3), $\delta = 6.50\text{--}7.88$ (m, 4H; C_6H_4), 6.05 (d, 1H; CH-U), 5.38 (m, 2H; CH=CH), 5.12-5.95 (m, 3H; $\text{CH}_2=\text{CH-}$), 3.00 (d, 2H; CH_2), 1.80-2.12 (br. m, 2H; CH_2), 1.20 (br.s, 10H; CH_2), 0.83 (br.t, 3H; CH_3).

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