

The Relationships between the structural difference of Norlignans and Coloration

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Japanese cedar (*Cryptomeria japonica* D. Don), Sugi, its timber has been extensively used. It is commonly said that the norlignans (C_{17} phenolic compounds) of Sugi wood are closely related to the coloration. The structure of norlignans related to the coloration of Sugi wood was studied. Squirin-C was converted by air oxidation or weak alkaline condition to the dark colored substance. While, likely structural compounds, hydroxysugiresinol (with pyran ring), cryptoresinol (with hydrofuran ring) and dihydrosequirin-C were converted to the pale colored substances. From the results, it was suggested that little structural difference of norlignans caused wide difference in coloration.

1. INTRODUCTION

Japanese cedar (*Cryptomeria japonica* D. Don) commonly called Sugi, grows well almost all over Japan. In the Japanese industry, Sugi is highly valued in all respects.

Its timber has been extensively used in the construction of Japanese houses. Especially, the heartwood color is one of commercial value. Heartwood color of normal Sugi is beautiful like salmonpink, but abnormal color due to darkness and blackness is not desirable by the people.

It is commonly said that the phenolic compounds of wood are closely related to the coloration. Sugi heartwood phenols which are related to the heartwood color were investigated.

Kai et al. [1-4] and ourselves [5,6] have isolated sugiresinol, hydroxysugiresinol, agatharesinol, sequirein-C and cryptoresinol, called as norlignans (C_{17} phenolic compounds). Main norlignans of Sugi are shown in Figure-1.

In this paper, the structural difference of norlignans and their significance to coloration is described.

2. EXPERIMENTAL

2.1. Extraction and isolation

Milled heartwood of Sugi (1kg) collected in Yamagata University Forest (Japan) was extracted with boiling methanol. The methanol extract was concentrated and extracted again with n-hexane. The insolubles were chromatographed on a column of silica gel using a mixture of n-hexane and acetone (1:1) as the eluting solvent.

Agatharesinol and sequirein-C were isolated, and these identifications were confirmed by direct comparison with authentic samples.

2.2. Air oxidation on silica gel plate

Squirin-C (5mg) and dihydrosequirin-C (5mg) were applied to a TLC plate and left in the laboratory. After 10 days, the colored bands were separated and extracted with methanol. The methanol solutions (10ml) were subjected to the UV-Visible spectrophotometer (Shimadzu UV-1600PC). The results are shown in Figure-3.

2.3. Treatment of weak alkaline

Squirin-C (5mg) was treated with weak alkaline solution (1% $KHCO_3$, 50ml, pH; 8.4). After one hour, the colored solution was subjected to the UV-Visible spectrophotometer (Shimadzu UV-1600 PC).

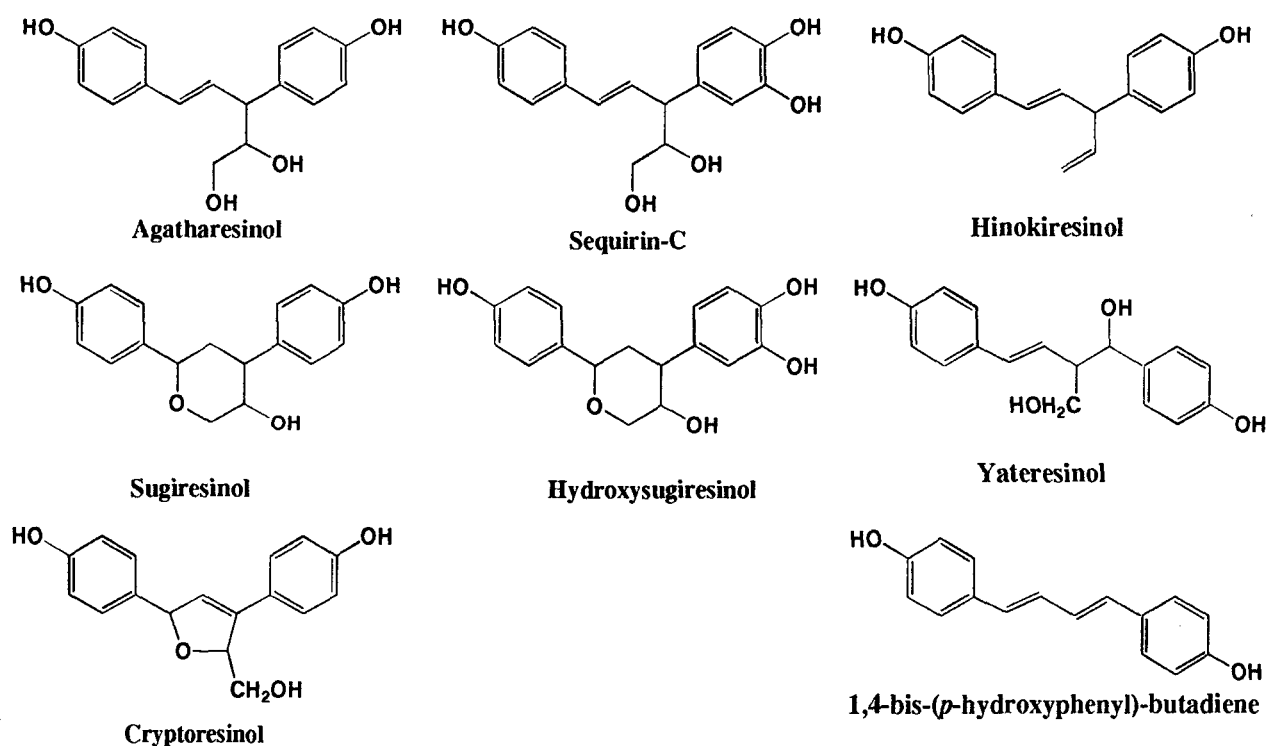


Fig.1 Norlignans of Sugi (*Cryptomeria japonica* D.Don)

2.4. Catalytic reduction of sequirin-C

Sequirin-C in ethanol was shaken with 5% Pd-C catalyst in an H₂ atmosphere at room temperature for one hour. The recovered material was subjected to preparative TLC to give the hydrogenated product dihydrosequirin-C.

Dihydrosequirin-C.

Gum; UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 224 (4.09), 281 (3.61). IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3350, 1620, 1519, 1448, 1398, 1221, 1129, 1104, 1052, 998, 926, 883, 824, 780, 737. ¹HNMR (400MHz, CD₃OD): δ (ppm) 1.94 (2H, *m*), 2.30 (1H, *m*), 2.36 (1H, *m*), 2.59 (1H, *m*), 3.28-3.34 (1H), 3.45 (1H, *dd*, *J*=4.1, 11.0Hz), 3.75 (1H, *m*), 4.85 (5H, *s*, OH), 6.57-6.92 (7H, aromatic H).

Dihydrosequirin-C pentaacetate.

¹HNMR (400MHz, CDCl₃): δ (ppm)

1.98, 1.99 (each 3H, *s*, alcoholic OAc), 2.28 (3H, *s*, aromatic OAc), 2.29 (6H, *s*, aromatic OAc), 1.95-2.02 (2H, *m*), 2.44 (1H, *m*), 2.54 (1H, *m*), 2.89 (1H, *m*), 3.93 (1H, *dd*, *J*=6.8, 12.0Hz), 4.16 (1H, *dd*, *J*=3.4, 12.0 Hz), 5.32 (1H, *m*), 6.97 (2H, *d*, *J*=8.3Hz, aromatic H), 7.05-7.10 (4H, aromatic H), 7.16 (1H, *J*=8.3, aromatic H).

¹³CNMR: δ (ppm) 32.4, 33.1, 45.3, 63.8, 73.1, 121.5 (2C), 123.3, 123.9, 126.6, 129.4 (2C), 138.2, 138.7, 141.1, 141.9, 148.9, 20.7 (3C), 20.8, 21.1, 168.0, 168.2, 169.6, 170.3, 170.6 (OAcx5).

3. RESULTS AND DISCUSSION

3.1. Air oxidation and enzymic oxidation.

It has been reported by Kai et al. that hydroxysugiresinol converted to a colored substance, dehydrohydroxysugiresinol having ortho-quinone structure (UV $\lambda_{\text{max}}^{\text{MeOH}}$ 410 nm),

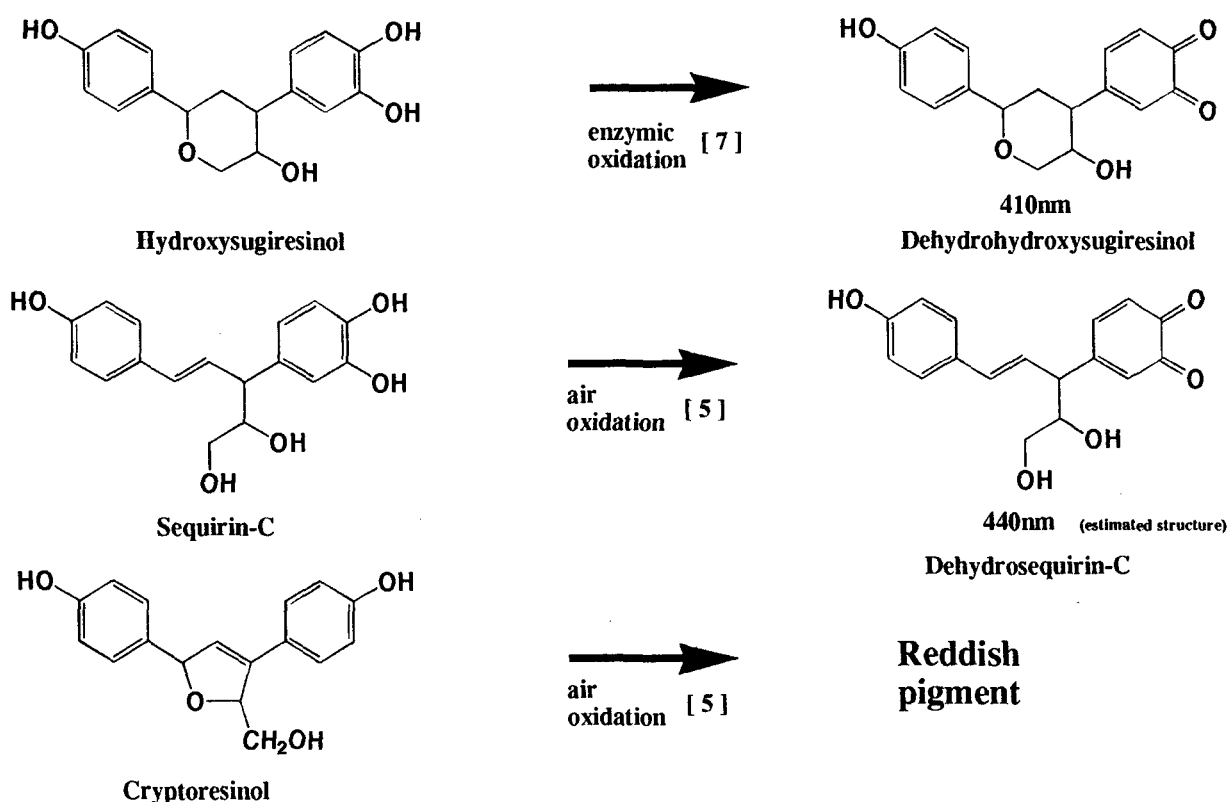


Fig.2 Coloration of norlignans

by enzymatic oxidation [7]. The author found that sequirin-C and hydroxysugiresinol were converted by air oxidation to the colored substances (dark brown pigment) which indicated a clear absorption maximum at 440nm, and cryptoresinol was to the bright red [5]. Shown in Figure-2.

3.2. Air oxidation of dihydrosequirin-C

Squirin-C and the hydrogenated product, dihydrosequirin-C converted to colored substances by air oxidation on TLC plate. The pigment from sequirin-C showed a clear absorption maximum at 440nm, while, the pigment from dihydrosequirin-C (free from double bond) did not show a clear absorption spectrum in visible (Figure-3).

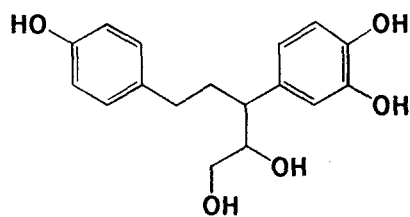
3.3. Weak alkaline treatment of sequirin-C

Squirin-C changed to dark purple. The

pigment from sequirin-C showed a absorption maximum at 510nm, and shoulder at 450nm and 652nm (Figure-4). While, dihydrosequirin-C did not change to the pigment at first, and later changed to pale purple.

Based on these results, it was found that sequirin-C having a double bond involved in a styryl chromophore and the catechol unit easily converted to colored substance by air or enzymic oxidation and weak alkaline treatment, respectively.

While, dihydrosequirin-C (free from double bond) difficultly converted to colored substance by air oxidation and weak alkaline treatment. Further, it was found that hydroxysugiresinol (with pyran ring) and cryptoresinol (with hydrofuran ring) converted by air or enzymic oxidation to pale pigments.



Dihydrosequirin-C

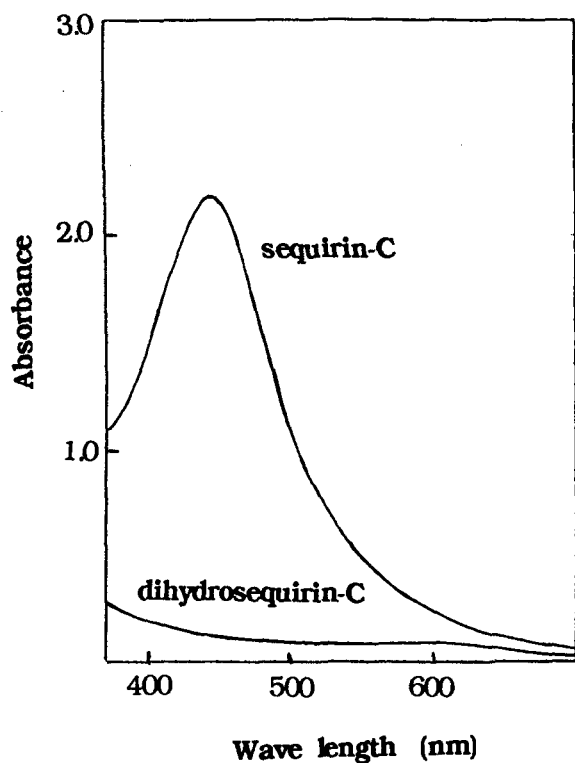
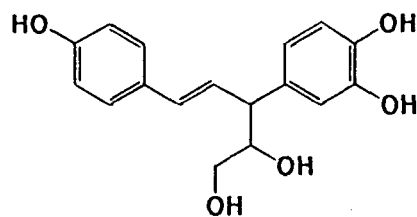


Fig3 Absorption spectra of colored substances obtained from sequirin-C and dihydrosequirin-C by air oxidation.

Thus, it was suggested that little structural difference of norlignans caused wide difference in coloration. Especially, not only the catechol unit but also the styryl structure influenced coloration of norlignans

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Sequirin-C

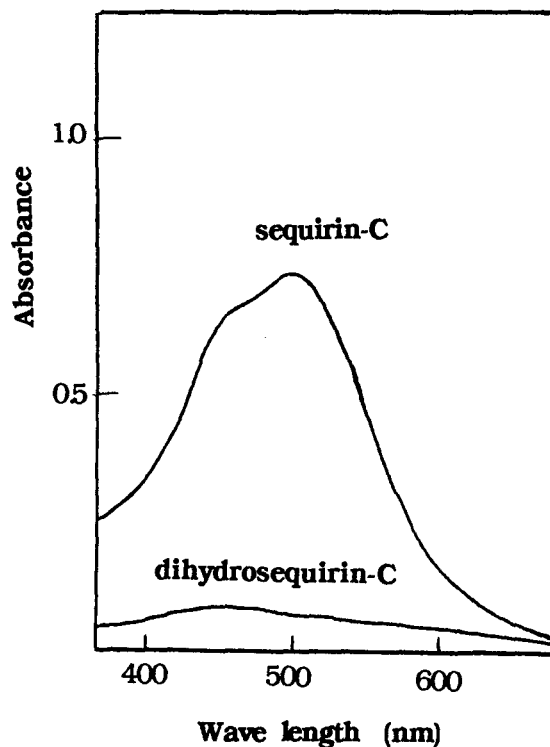


Fig4 Absorption spectra of colored substances obtained from sequirin-C and dihydrosequirin-C by weak alkaline treatment.

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