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BIOTRANSFORMATION OF FOREIGN SUBSTRATES WITH CALLUS TISSUES. TRANSFORMATION OF TERPINEOLS WITH TOBACCO SUSPENSION CELLS

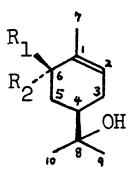
Takayuki SUGA, Tadashi AOKI, Toshifumi HIRATA, Ym Sook LEE,
Osamu NISHIMURA, and Masafumi UTSUMI
Department of Chemistry, Faculty of Science, Hiroshima University,
Higashisenda-machi, Hiroshima 730

Biotransformation of foreign substrates with the suspension cells of *Nicotiana tabacum* was tested with α-terpineol (I), *trans*-β-terpineol (II), and *trans*-β-terpinyl acetate (III). It was found that the cultured cells have the ability to hydroxylate the C-C double bond itself as well as its allylic positions.

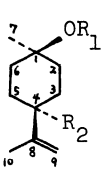
The ability of callus tissues to metabolize or transform biologically foreign substrates is considerably interest.[1-3] We recently found that the tobacco suspension cells hydroxylate the *trans*-methyl group in the isopropylidene group of linalool and its derivatives.[3] We now have examined the transformation of cyclic monoterpenoids having an *endo*-cyclic and a terminal C-C double bonds, and found the new facts differing from the case of the acyclic monoterpenoids. We here wish to communicate these findings.

Tobacco callus tissues were derived from the stem of *Nicotiana tabacum* "Bright Yellow." The feeding experiment and the working-up were carried out in the same manner as described in our previous paper.[3] The administration of α-terpineol (I), *trans*-β-terpineol (II), and *trans*-β-terpinyl acetate (III) to the suspension cells gave the hydroxylated products as shown in Table 1. These products were identified on the ground of interpretation of their spectral data and direct comparison of TLC, GLC, and spectral data with authentic samples.[4-6]

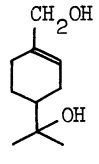
It was found that glycol IX was a major product in the biotransformation of III. This indicates that the cultured cells have the ability to hydroxylate the C-C double bond itself. It was further clarified that the cells hydroxylate chiefly the carbon atoms allylic to the C-C double bond of the terpineols.



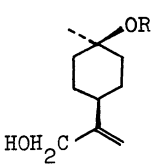
I: $R_1=R_2=H$
V: $R_1=H$, $R_2=OH$
VI: $R_1=OH$, $R_2=H$



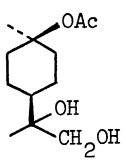
II: $R_1=R_2=H$
III: $R_1=Ac$, $R_2=H$
VIII: $R_1=H$, $R_2=OH$
XI: $R_1=Ac$, $R_2=OH$



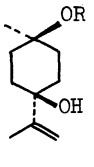
IV



VII: R=H
X: R=Ac



IX



XII: R=H
XIII: R=Ac

Table 1. Biotransformation of terpineols, I, II, and III, by *Nicotiana tabacum* suspension cells

Substrates	Products	Yield (%)*
α-Terpineol (I)	7-Hydroxy-α-terpineol (IV)	15.0
	trans-6-Hydroxy-α-terpineol (V)	5.9
	cis-6-Hydroxy-α-terpineol (VI)	3.9
trans-β-Terpineol (II)	10-Hydroxy-*trans*-β-terpineol (VII)	13.1
	4-Hydroxy-*trans*-β-terpineol (VIII)	6.1
trans-β-Terpinyl acetate (III)	8,9-Dihydroxy-*trans*-β-terpinyl acetate (IX)	14.7
	10-Hydroxy-*trans*-β-terpinyl acetate (X)	9.8
	4-Hydroxy-*trans*-β-terpinyl acetate (XI)	8.4

* The weight percent of the products per the administered substrates.

The allylic hydroxylation taking place in the cyclic monoterpenoids with an *endo*-cyclic and a terminal double bonds was less selective than the case in the acyclic monoterpenoids.[3] The hydroxylation of the 4-methine group of II and III occurred stereospecifically, affording only *trans*-isomers, VIII and XI, and no *cis*-isomers, XII and XIII, respectively. Tahara *et al.*[6] observed the fact that the SeO_2 oxidation of III produced 4-hydroxy-*trans*-β-terpinyl acetate (XI) and its *cis*-isomer (XIII) in the ratio of 6:5. Therefore, the hydroxylation of II and III with the tobacco suspension cells were found to be more stereoselective than with SeO_2.

Thus, it is fascinating to note the facts as follows; (i) the tobacco cells have the ability to hydroxylate the C-C double bond itself as well as its allylic positions, and (ii) the hydroxylation of 4-methine group of β-terpineol and its acetate is stereospecific.

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