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BIOSYNTHESIS OF ISOPRENOID FROM AMINO ACID IN HIGHER PLANT. INCORPORATION OF L-VALINE INTO LINALOOL

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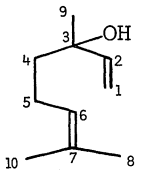
L-[U-^{14}C]Valine was incorporated into linalool (I) in *Cinnamomum Camphora* Sieb. var. *linalooliferum* Fujita with 0.0055% at the highest value. The labeling pattern indicated that some of 3,3-dimethylallyl pyrophosphates originate from valine *via* an alternative route rather than through the mevalonoid pathway.

Recently we proposed the possibility of a non-mevalonoid route for the biosynthesis of linalool from leucine in the higher plant.[1] Investigating further on this line, we examined the incorporation of L-[U-^{14}C]valine into linalool (I) in *Cinnamomum Camphora* Sieb. var. *linalooliferum* Fujita. Here we report evidence for the participation of L-valine in the biosynthesis of linalool.

The labeled valine was given to the terminal branches of the plant.[2] The data presented in Table I demonstrate that L-^{14}C-valine was incorporated into I. Further, the results show that I was synthesized biologically from L-valine more actively in July than in October. The radioactive linalool isolated was degraded[2] to 4-methyl-4-hexanolide (II) and acetone, and further purification of these to constant radioactivity (Table 2) was effected by their conversion to the S-benzylthiouronium salt and thiosemicarbazone derivatives, respectively. The distribution of the radioactivity in the 3,3-dimethylallyl pyrophosphate (DMAPP) moiety of I is upon the C_3-fragment (isopropylidene group) representing 3/5 of the prenyl unit. The distribution in the isopentenyl pyrophosphate (IPP) unit is, in turn, calculated by the difference, as shown in Table 3. Sixty to seventy per cent of the total radioactivity in I was located in the DMAPP moiety when L-[U-^{14}C]valine was given, whereas the predominant radioactivity was distributed in the IPP moiety when [2-^{14}C]mevalonate (MVA) was administered.[1] If linalool (I) is synthesized from valine *via* MVA, the labeling pattern should be similar to the pattern in I which was synthesized from [2-^{14}C]MVA. The unbalanced distribution of the tracer



I

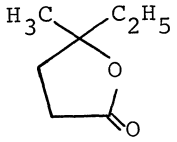


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TABLE 1. INCORPORATION OF L-[U-^{14}C]VALINE INTO LINALOOL (I)

Exp. No.	L-[U-^{14}C]Valine (mCi)	Feeding time (hr)	Seasons	Specific radioactivity of I (dpm/mmole)	Incorporation (%)
1	0.01	24	July	7.52×10^2	0.0055
2	0.005	12	October	5.92×10^2	0.0015
3	0.02	24	"	2.72×10^2	0.0015
4	0.005	36	"	5.42×10^2	0.0012

TABLE 2. DISTRIBUTION OF RADIOACTIVITY IN LINALOOL (I) AFTER THE UPTAKE OF L-[U-^{14}C]VALINE

Compounds (Carbons originated from I)	Specific radioactivity* (dpm/mmole)	
	Exp. 1	Exp. 3
Linalool (I) (C-1~C-10)	7.52×10^2	2.72×10^2
Thiosemicarbazone of acetone (C-7, C-8, and C-10)	3.17×10^2	1.06×10^2
S-Benzylthiouronium salt of lactone II (C-1~C-6 and C-9)	4.36×10^2	1.69×10^2

* "Exp. No." corresponds to the number in Table 1.

TABLE 3. DISTRIBUTION OF RADIOACTIVITY IN IPP AND DMAPP MOIETIES

IPP and DMAPP moieties of I	Distribution (%)*	
	Exp. 1	Exp. 3
IPP	29.8	35.6
DMAPP	70.2	64.4

* "Exp. No." corresponds to the number in Table 1.

in favor of the DMAPP moiety is rationalized by assuming that some of the DMAPPs have directly originated from valine by an alternative route rather than through the mevalonoid pathway. This is compatible with our proposal[1] for the possibility of the non-mevalonoid route in the biosynthesis of the monoterpene from amino acid. For the generation of DMAPP from valine, we now wish to propose a pathway involving deamination of valine to produce dimethylacrylic acid, reduction of the acid to give 3,3-dimethylallyl alcohol, and then phosphorylation of the alcohol to yield DMAPP.

Reference and Note

1) T. Suga, T. Hirata, T. Shishibori, and K. Tange, Chem. Lett., 1974, 189.

2) Feeding experiments and degradation of labeled linalool (I) were carried out by the same procedures as described in our previous paper.[1]

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