

Wang^{1,2} and Strittmatter^{3,4} demonstrated the presence of different acid phosphatase activities in the soluble and in the particulate fractions of the liver of chicken at different development stages. These authors concluded that 2 molecular forms of acid phosphatase, at least, must exist in the liver of the developing chick. Preliminary results, obtained in our laboratory, demonstrate that the 'soluble' phosphatase constitutes the most rapid electrophoretic band, and the other 2 phosphatases are present in the particulate fraction.

The electrophoretic patterns of alkaline phosphatases of liver, heart and intestine of the chick are reported in figure 2. In the left photograph (2, a) is shown the electrophoresis carried out at pH 8.5. While 2 enzyme fractions appear in the samples of liver and heart, a very diffuse band is shown by the intestine. When the analysis is carried out at pH 7.5, this band is resolved into 2 fractions, as shown in figure 2, b. In these conditions, the alkaline phosphatases of liver and heart are not isolated on the gels. This electrophoretic behaviour demonstrates a difference between the molecular forms of alkaline phosphatase of intestine and those of liver and heart. The finding of 2 molecular forms of alkaline phosphatases in the intestine of the adult chick confirm the results of Chang and Moog⁵ concerning 1-day-old chicken.

The results reported here are also in agreement with the data concerning the molecular multiplicity of acid and alkaline phosphatases of liver and intestine of other verte-

brates. In all cases, no more than 3 or 4 molecular forms of acid^{6,8-11} and alkaline¹²⁻¹⁴ phosphatase have been described. Works are in progress to confirm the homogeneity of the electrophoretic fractions, to describe the function properties of each molecular form and to determine their subcellular localization.

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Formation of enantiomeric sesquiterpenes in the secretions of scale insects

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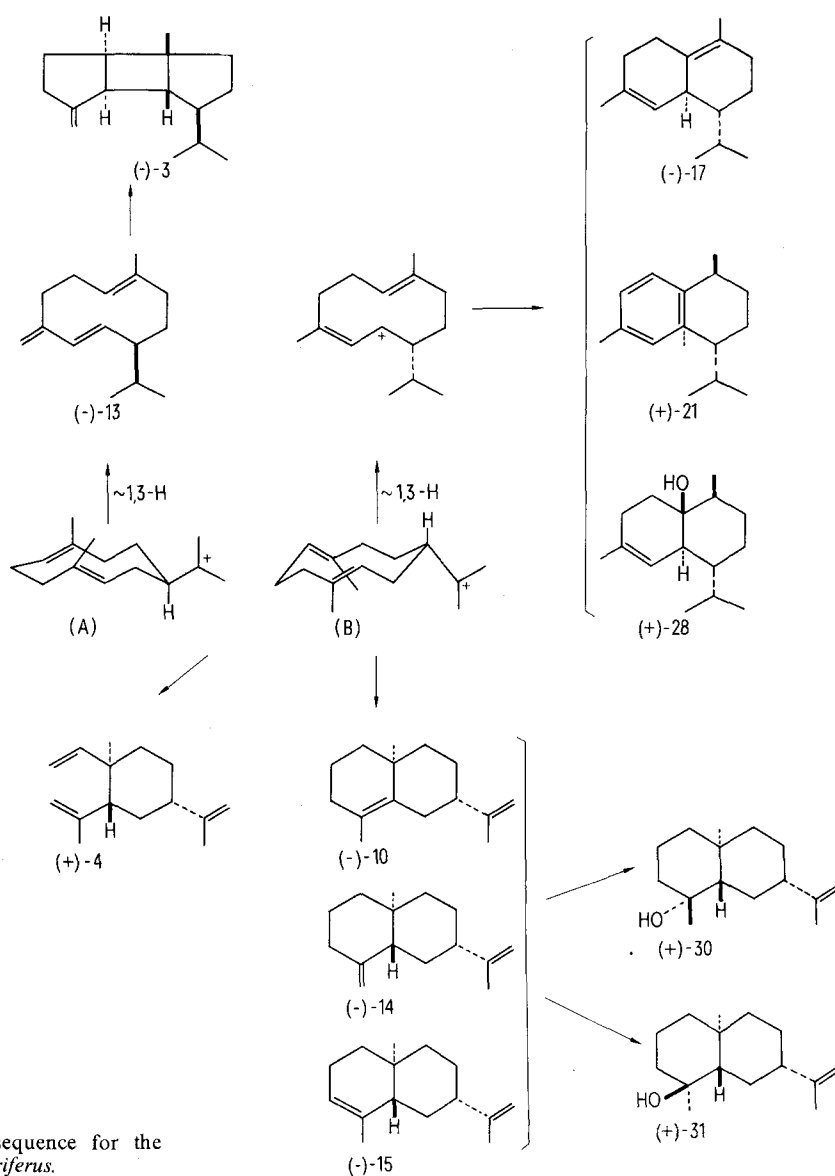
Summary. The volatile oil present in the secretion of a scale insect, *Ceroplastes ceriferus* Anderson (fam. Coccidae), has been found to consist of a number of sesquiterpenes which are enantiomeric with respect to those from *C. rubens* Maskell, which infests the same host tree. The present investigation strongly suggests that each insect possesses a specific set of C-C cyclases for the sesquiterpenoids.

The scale insects *C. ceriferus* and *C. rubens* infest over 10 species of trees and exude odoriferous waxy secretions in which they become encrusted. The secretions contain volatile oils which may serve as plasticizers of the waxy resins. We have examined the compositions of the volatile oils and found sesquiterpenes to be the major components, as shown in the table. Comparative examination of the volatile oils from *C. ceriferus* on 7 different species of host trees (*Diospyros Kaki*, *Liquidambar formosana*, *Spiraea cantoniensis*, *Zelkova serrata*, *Ilex rotunda*, *Camellia japonica* and *Acer palmatum*) and from *C. rubens* on 2 different species of host trees (*Camellia japonica* and *Laurus nobilis*) has shown that their constituents are independent of the species of host trees and are specific to the insects.

Materials and methods. The general procedure used will be illustrated here by means of a specific example, as follows. *C. ceriferus* (487 g) fed on the host *Diospyros Kaki* Thunb. was collected in Tokushima Prefecture, Japan, in January. The secretion was washed off with ether and was separated from insect debris (83 g). The slurry was evaporated in vacuo and the residue was steam-distilled to give the volatile oil, 2.38 g (0.59% of the secretion). On the other hand, *C. rubens* (53 g) gave volatile oil, 0.12 g, in a yield of 0.25% from its secretion. Each oil was analyzed by GC-MS, then the components were isolated by column chromatography using silver nitrate-impregnated silica gel and by

preparative gas chromatography (Carbowax-20 M and Thermo-1000). The isolated compounds were identified by MS- and IR-spectrometry, and when possible, optical rotations were measured. To confirm the absolute configurations, the compounds numbered 3, 4, 14 and 15 in the table were hydrogenated to the corresponding skeletal hydrocarbons (No. 32, 33 and 34 in the table) and their optical rotations were compared with the reported values. Compounds No. 30 and 31 were dehydrated with SOCl₂-Py to yield compounds No. 10, 14 and 15 and then hydrogenated to selinane (No. 34).

Results and discussion. It is noteworthy that sesquiterpenes secreted by *C. ceriferus* belong to the optically antipodal series compared to those of *C. rubens* on the same host tree, as shown in the table. Moreover, our results indicate that only germacrene-D and β -bourbonene (No. 13 and 3, respectively, in the table) possess isopropyl groups epimeric to those of the rest of the compounds in both secretions. β -Bourbonene can be formed³ very easily by photoreaction from germacrene-D, so their isopropyl groups naturally have the same configuration. Germacrene-D, with the isopropyl group epimeric to those of cadinene-, selinene- and elemene-type sesquiterpenoids, evidently cannot be a key intermediate in their formation. Therefore, 2 precursors corresponding to the epimeric isopropyl groups should exist. In addition, the sesquiterpenes other than germa-



Hypothetical biogenetic sequence for the sesquiterpenes from *C. ceriferus*.

Compounds identified in the secretions of *C. ceriferus* and *C. rubens*

Constituents	Content on GLC		[α] _D Obs. in CHCl ₃ *		Lit. value** (Ref.)
	<i>C. ceriferus</i>	<i>C. rubens</i>	<i>C. ceriferus</i>	<i>C. rubens</i>	
1. Linalool	+				
2. α -Copaene	+	+			
3. β -Bourbonene	+	+	- 82°	+ ***	- 92° ⁸
4. β -Elemene	+	++	+ 18°	- 16.9°	- 20°
5. β -Elemene (epimer)	+	+			
6. Caryophyllene	++				
7. Aromadendrene		+			
8. C ₁₅ H ₂₄		+			
9. α -Humulene	+++	+			
10. Selina-(4,5),11-diene		+	- 49°		+ 13.8° ⁹
11. α -Muurolene		+			
12. γ -Muurolene	+				
13. Germacrene-D	++	++	- 263°	+ 235°	- 240° ³
14. β -Selinene	+	++	- 85°	+ 60°	+ 48°
15. α -Selinene	+	+	- 0.5°		+ 63°
16. C ₁₅ H ₂₄		+			
17. δ -Cadinene	++	+	- 88°	+ ***	+ 89°
18. α -Curcumene		+			
19. Selina-3(7,11)-diene	+				

Table continued

Compounds identified in the secretions of *C. ceriferus* and *C. rubens*

Constituents	Content on GLC <i>C. ceriferus</i>	<i>C. rubens</i>	[α] _D Obs. in CHCl ₃ * <i>C. ceriferus</i>	<i>C. rubens</i>	Lit. value** (Ref.)
20. Cadina-1,4-diene	+	+			
21. Calamenene	+		+ 54°		— 67° ¹⁰
22. C ₁₅ H ₂₄ O		+			
23. α -Calacorene	+				
24. β -Calacorene	+				
25. Caryophyllene-oxide	+				
26. Humulene-epoxide-I	+				
27. Humulene-epoxide-II	+				
28. Cubenol	+	+	+ 37°		— 24.8° ¹¹
29. Epi-cubenol	+	+			
30. Neointermedeol	+	+	+ 3.4°		+ 8° ¹²
31. Seli-11-en-4(α)-ol	+		+ 32.7°		— 18° ¹³
Standards (see text)					
32. Dihydrobourbonene			— 7.7°		— 6.4° ⁸
33. Elemene			+ 5°		— 4.8°
34. Selinane			— 20°		+ 12.5°

* Since the optical rotations of the same compounds from a given insect on different host trees were nearly the same, the highest rotations were adopted. ** Unless otherwise referenced, the optical rotations are taken from Beilstein. *** Only the sign was observed at 589, 546, 436 and 365 nm, because of the limited sample size.

crene-D and β -bourbonene from *C. ceriferus* were of the enantiomeric series compared with those from common terrestrial plants^{4,6}.

During the last decade, the presence of some cedrene-type sesquiterpenoids was reported in the scale insect *Laccifer lacca* Kerr⁷. As regards the origin of these substances, it seems very likely that they are metabolites of vegetable origin. Though the biosynthetic route to sesquiterpenoids in *C. ceriferus* and *C. rubens* is not yet known, it seems reason-

able to conclude from the present results that each insect possesses a different set of enzymes acting in the cyclization process to produce epimeric isopropyl groups. Therefore, these insects can presumably synthesize sesquiterpenoids at least from the stage of cyclization to produce a pair of 10-membered cyclic intermediates such as A and B in the hypothetical route shown in the scheme. Enzymatically controlled 1,3-hydride shift to the cationic center on the isopropyl group may then lead to the end products.

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Glutathione peroxidase in erythrocytes and plasma of rats during pregnancy and lactation¹

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Summary. The glutathione peroxidase activity in the plasma of rats on the 20th day of pregnancy was found to be 50% lower than in nulliparous control animals. During lactation, the level rose again but was still significantly different from that of the control rats on the 20th day post partum. The erythrocyte enzyme activity remained unchanged.

The selenium metabolism of rats was found to be affected after mid-pregnancy. In the serum, the element content began to drop on the 12th day of gestation and reached its lowest value shortly before term^{4,5}. During lactation, it rose again to its original level. When ⁷⁵Se-selenite was administered to rats, a significant decrease in the ⁷⁵Se-radioactivity in the erythrocytes was observed at the end of pregnancy as compared with nulliparous controls⁶. Because of the presence of selenium in glutathione peroxidase (GSH-Px)^{7,8}, it

was of interest to investigate whether the metabolism of this enzyme is also influenced during the reproductive processes in female rats. Therefore the GSH-Px activity in the plasma and erythrocytes was measured during pregnancy and lactation.

Experimental. The study was carried out under the same conditions as described earlier⁵: 20 female 'Carworth' rats with body weights of 250 g were kept under standardized laboratory conditions and fed Altromin® rat pellets with a