

hydrochloride. (Found: C 11.00; H 3.67. M.p. 172–74°C. Calc. for  $C_2H_8Cl_2N_4S_2$ : C 10.76; H 3.61). The unsubstituted formamidine disulfide dihydrochloride was also obtained when *tert*-butylformamidine disulfide dihydrobromide was heated with conc. hydrochloric acid to 80°C for 1½ h and then to 100°C for 5 min. The infrared spectra of these two samples were identical with the spectrum of an authentic sample of formamidine disulfide dihydrochloride.

The melting points were determined in capillary tubes with a heating rate of 2–3°C/min.

In conclusion it should be mentioned that the melting point of *tert*-butylthiourea was found to be 181–181.5°C, *i.e.* considerably higher than the values given in the literature (168<sup>7</sup>: 171–72<sup>8</sup>). (Found: C 45.43; H 9.15; N 21.16. Calc. for  $C_8H_{12}N_2S$ : C 45.44; H 9.15; N 21.20).

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## The Structure of (+)- $\epsilon$ -Muuro- lene (" $\epsilon$ -Cadinene") \*,\*\*

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Four sesquiterpenes of the cadalene type yielding (+)-muurolene dihydrochloride<sup>1</sup> (m.p. 87–8°,  $[a]_D^{22} + 13.2^\circ$  (c 1.5) \*\*\*) have been isolated from the wood of *Pinus silvestris* L. as well as from the fraction b.p. 100–140°/10 mm of Swedish sulphate turpentine. Two of them, "muurolene-I" and "muurolene-II"† ( $C_{15}H_{24}$ , b.p. 125–7°/10 mm,  $n_D^{22}$  1.5059,  $[a]_D^{22} - 1.8^\circ$  (c 2.5);  $C_{15}H_{24}$ , b.p. 128–30°/10 mm,  $n_D^{22}$  1.5063,  $[a]_D^{22} - 85.3^\circ$  (c 2.3), respectively) appear not to have been previously isolated in the pure state (*cf.* Refs.<sup>1-3</sup>). Spectral data (IR, NMR) indicate a close relationship with the cadinenes and also that "muurolene-I" possesses one trisubstituted and one exocyclic double bond and that "muurolene-II" has two trisubstituted double bonds. Attempts to determine the positions of the double bonds in these compounds are being made.

A third component yielded (+)-muurolene dihydrochloride and (–)-cadinene dihydrochloride (ratio: 1:6), and has been identified as copaene (IR, various physical constants and conversion to the diol<sup>4</sup> prepared by Büchi *et al.*††). A mixture of the same dihydrochlorides (ratio 3:1) was also formed from the fourth hydrocarbon, which was shown to be identical with the so called " $\epsilon$ -cadinene" (IR, refractive index, optical rotation<sup>5</sup>) for which structure (1) has been proposed by Šýkora, Herout and Šorm.<sup>6</sup>

\* The Chemistry of the Natural Order Pinales, Part 34. Part 33: *Acta Chem. Scand.* **17** (1963) 2351.

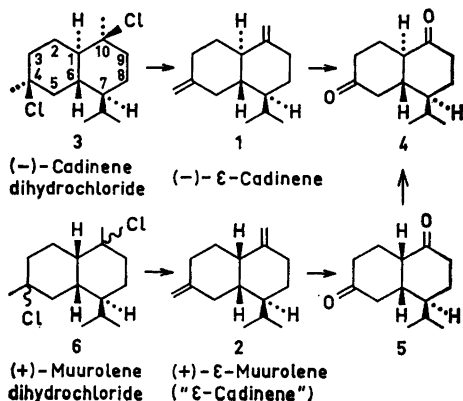
\*\* Presented at "Ekmandagarna" 21 January, 1964, Stockholm.

\*\*\* Rotations were taken in chloroform.

† Provisional names. Aschan<sup>1</sup> isolated a sesquiterpene fraction from an industrial extract of resinous pine stumps (*Pinus silvestris*) produced in Muurola, Finland, which he called "muurolene".

†† I thank Professor G. Büchi for a generous gift of copaene.

It has now been found that the structure of "ε-cadinene" is (2) containing *cis*-fused rings and not (1) with *trans*-fused rings. An unfortunate consequence of this structural revision is the fact that the name "ε-cadinene" is misleading. It therefore appears necessary to introduce a new name for this sesquiterpene and it is proposed that, in the future, the sesquiterpene hitherto known as "ε-cadinene" should be called (+)-ε-muurolene. When the structures of "muurolene-I" and "muurolene-II" have been elucidated, these compounds should be named α-, β-, etc. muurolene by analogy with the naming in the cadinene series.<sup>7\*</sup> The name (-)-ε-cadinene should be used for compound (1).



The latter sesquiterpene has not yet been isolated from any natural source but it has now been prepared from (-)-cadinene dihydrochloride.

When (-)-cadinene dihydrochloride (3) was treated with potassium triethyl carbinolate, a base with considerable steric requirements,<sup>8</sup> an olefinic mixture containing 40 % of (-)-ε-cadinene (1) was obtained. This compound was isolated by column chromatography on silver nitrate-silica gel<sup>9</sup> and proved to be homogeneous by gas-liquid (GLC) and thin layer chromatography on silver nitrate-silica gel (Ag-TLC).<sup>9,10</sup>

The IR-spectrum of this hydrocarbon (C<sub>15</sub>H<sub>24</sub>, [α]<sub>D</sub><sup>22</sup> -15.9° (c 1.5), n<sub>D</sub><sup>22</sup> 1.5032) was essentially identical with that of (+)-ε-muurolene (2) in the 3200–1350 and 900–870

\* The muurolenes may thus be defined as 1-*epi*-cadinenes.

cm<sup>-1</sup> regions but there were considerable differences in the 1350–900 cm<sup>-1</sup> region. (-)-ε-Cadinene (1) was ozonised in methylene chloride at -80°, followed by treatment with water at 90° to yield a crystalline diketone, m.p. 99–101°, [α]<sub>D</sub><sup>22</sup> -40.2° (c 1.1). This diketone (4) (m.p. 103°, optical rotation not reported) has been prepared from (+)-ε-muurolene ("ε-cadinene") (2) by Herout *et al.*<sup>11</sup> (for syntheses, cf. Refs.<sup>12,13</sup>).

When a sample of (+)-ε-muurolene (2) isolated from Swedish sulphate turpentine ([α]<sub>D</sub><sup>22</sup> +50.7° (c 2.2), n<sub>D</sub><sup>22</sup> 1.5049) was ozonolysed under the conditions used by the Czech authors (ozonisation in ethyl acetate at 0° and decomposition of the ozonide with water at 100°; the purification was carried out by means of chromatography on alumina instead of magnesia) the same crystalline diketone (4) was obtained.

When, however, the ozonisation was carried out in methylene chloride at -80° followed by decomposition of the ozonide with water at 90° and purification of the product by rapid chromatography on deactivated silica gel the oily diketone (5) [α]<sub>D</sub><sup>22</sup> +73.8° (c 0.9) was isolated as the main product.

When this diketone was heated with 1 % sulphuric acid in 70 % aqueous acetic acid at 90° for 2 h it furnished the above crystalline diketone (4) in almost quantitative yield. This transformation is obviously due to epimerisation at C-1.

When treated with potassium triethyl carbinolate (+)-muurolene dihydrochloride (6) gave an olefinic mixture containing 20 % (+)-ε-muurolene (2). Ag-TLC showed that the crude mixture contained only a trace of (-)-ε-cadinene (1).

These results show that the dehydrochlorination of (+)-muurolene dihydrochloride to (+)-ε-muurolene as well as that of (-)-cadinene dihydrochloride to (-)-ε-cadinene proceeds without inversion at C-1. Thus (-)-ε-cadinene must have the configuration shown in formula (1).

This fact combined with the results of the ozonolysis experiments proves that (+)-ε-muurolene (previously "ε-cadinene") must possess structure (2).

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## A Simple Test for Amines

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At this institute, a general test for amines has been found valuable and has been used successfully at student courses during the past twelve years.

To 0.03 ml (base) or 20–30 mg (base or salt) of the sample in a test tube is added 0.06 ml (2 drops) of water, 1 ml of diethyl ether and 300–500 mg of anhydrous sodium carbonate. The tube is stoppered and is shaken vigorously for half a minute. The clear ethereal solution is decanted carefully into a small test tube containing 1 ml of a saturated solution of anhydrous oxalic acid in dry diethyl ether (8 g/100 ml). An immediate precipitate

— often crystalline — indicates the presence of an amine or a salt of an amine in the unknown sample.

The test gives positive results with any amines — aliphatic, aromatic or heterocyclic — provided the base is not too weak or of too low solubility in ether. Thus even such weak bases as *m*- and *p*-chloroaniline or *p*-nitrophenylhydrazine give a positive reaction, whereas extremely weak bases like *o*-nitroaniline, 2,4-dichloroaniline, 2,4-dinitrophenylhydrazine, diphenylamine, and carbazole do not react.

Due to the salting out effect of the sodium carbonate, several strongly hydrophilic amines such as ethylenediamine and ethanolamine give distinctly positive reactions.

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## $\alpha$ -Keto- $\delta$ -guanidinovaleriansäure und $\gamma$ -Hydroxy- $\alpha$ -ketoglutarsäure in grünen Teilen und Samen von *Phlox* Pflanzen

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Im Zusammenhang mit Untersuchungen des Stoffwechsels der Aminosäuren bei *Phlox decussata*<sup>1</sup> untersuchten wir auch das Vorkommen von Ketosäuren, da sie durch enzymatische reduktive Transaminierung mit Aminosäuren im Gleichgewicht stehen können.

Nach Isolierung der Ketosäuren aus Blättern oder Samen von *Phlox decussata* und Umsetzung mit Dinitrophenylhydrazin zu den Hydrazonen erhielten wir daraus durch Hydrogenolyse mit Zinn in alkoholischer Salzsäure (4°; 12 Stunden) die entsprechenden Aminosäuren,<sup>2</sup> die wir durch Papier- und Dünnschichtchromatographie auftrennten. Hierbei fanden wir neben den in den Pflanzen allgemein vorkommenden Ketosäuren: Glyoxylsäure (= 1. Glykokoll), Brenztraubensäure (= 2. Alanin), Hydroxybrenztraubensäure (= 8.

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