

solution of Ni dtp₂ in dichloroethane, some evidence can be found for the existence of high-spin Ni dtp₂en, since a band at 1100 m μ ($\epsilon \approx 18$) and a shoulder at 940 m μ are observed. The subsequent bands at 678 m μ ($\epsilon = 38$) and 525 m μ ($\epsilon = 32$) are probably caused, in part, by unreacted Ni dtp₂.

1. Jørgensen, C. K. *J. Inorg. Nucl. Chem.*
2. Jørgensen, C. K. *Acta Chem. Scand.* **16** (1962) 2017.
3. Stevenson, D. P. and Coppinger, G. M. *J. Am. Chem. Soc.* **84** (1962) 149.
4. Jørgensen, C. K. *Acta Chem. Scand.* **11** (1957) 399.
5. Jørgensen, C. K. *Z. anorg. Chem.* **316** (1962) 12.
6. Harris, C. M., Nyholm, R. S. and Phillips, D. J. *J. Chem. Soc.* **1960** 4379.
7. Barclay, G. A., Nyholm, R. S. and Parish, R. V. *J. Chem. Soc.* **1961** 4433.
8. Krebs, H., Weber, E. F. and Fassbender, H. *Z. anorg. Chem.* **276** (1954) 128.
9. Jørgensen, C. K. *Acta Chem. Scand.* **10** (1956) 887.
10. Jørgensen, C. K. *Advan. Chem. Phys.* **5** (1963) 33.
11. Jørgensen, C. K. *Progr. Inorg. Chem.* **4** (1962) 73.
12. Beck, M. T. and Bjerrum, J. *Acta Chem. Scand.* **16** (1962) 2050.

Received January 9, 1963.

Studies on the Degradation of Lignin and Model Compounds. I. The Configuration of Dehydrodi-isoeugenol

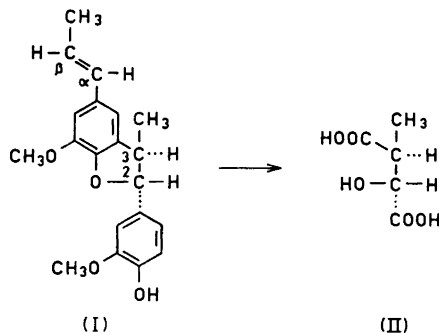
GUNHILD AULIN-ERDTMAN and YUTAKA TOMITA

Träkemiska Institutionen,

and (in part) STURE FORSÉN

Kärnresonansgruppen, Fysikalisk-kemiska Institutionen, Kungl. Tekniska Högskolan, Stockholm, Sweden

Dehydrodi-isoeugenol (I) was first obtained by Cousin and Hérissé in 1908 through oxidative coupling of isoeugenol¹. The structure was elucidated by Erdtman in 1933² and later confirmed³⁻⁵. A large



number of studies have since then been carried out on the properties and reactions of dehydrodi-isoeugenol, which is an important lignin model compound. Its configuration, however, has remained unknown, although it is of interest for the understanding of the mechanism of the coupling reaction.

We have now found by IR and PMR investigation that the side-chain of dehydrodi-isoeugenol has the *trans*-configuration. The compound shows a strong IR band at ca. 960 cm⁻¹, disappearing on hydrogenation of the side-chain, but no band at 710 cm⁻¹. *Trans*-isoeugenol absorbs⁶ at ca. 960 cm⁻¹ and *cis*-isoeugenol⁷ at ca. 710 cm⁻¹. The PMR spectrum (S. Forsén) of dehydrodi-isoeugenol in carbon tetrachloride solution (internal reference: tetramethyl silane) shows a doublet at $\delta = 1.83$ ppm, due to the methyl group of the side-chain. The spin coupling constant between the methyl protons and the proton at the β -carbon atom is 5.2 c/s. The coupling constant between the methyl protons and the proton at the α -carbon atom is less than 0.5 c/s. These values are in excellent agreement with the corresponding values found for *trans*-isoeugenol while for *cis*-isoeugenol the figures are 6.9 and 1.6 c/s, respectively.

We have found that, apparently, *cis*-isoeugenol does not give any dehydrodi-isoeugenol with ferric chloride. Using Leopold's procedure⁸, *trans*-isoeugenol gave a 30% yield of dehydrodi-isoeugenol, which crystallized during the reaction. A mixture of *trans*- and *cis*-isoeugenol (1:1) gave a 15% yield of dehydrodi-isoeugenol while *cis*-isoeugenol gave a non-crystalline product.

The configuration of the coumarane portion of dehydrodi-isoeugenol was determined by treating the compound with

ozone in acetic acid at room temperature for three days. The ozonides were decomposed with hydrogen peroxide. The β -methyl malic acid formed was extracted with ether from a pH 3.5–4 aqueous solution of the reaction products (in which the oxalic acid remained), and its di-*p*-bromophenacyl ester, $C_{21}H_{18}O_7Br_2$, was prepared and recrystallized from ethanol. The product (A) had a m.p. of 186–7°.

For comparison with product A, *erythro*- β -methyl malic acid di-*p*-bromophenacyl ester was prepared from *erythro*-1,2-diphenylpropanol⁹ in a similar way. The product (B) showed the m.p. 187–8°, which was undepressed on admixture of A.

Threo- β -methyl malic acid di-*p*-bromophenacyl ester was similarly prepared from *threo*-1,2-diphenylpropanol⁹. The product (C) melted at 101–3°.

The IR curves of A and B were superimposable while that of C was distinctly different.

The β -methyl malic acid (II) obtained from dehydrodi-iso Eugenol thus being the *erythro*-form, the substituents at the coumarane ring in the latter compound must be arranged as shown in formula (I) (*trans*-configuration).

PMR investigations (S. Forsén) of dehydrodi-iso Eugenol, 2,3-dibromocoumarane and dihydrocoumarilic acid showed that the spin coupling between protons attached to carbon atoms 2 and 3 of the oxygen ring is dependent not only on the configuration but also on the nature of the other substituents at those positions.

We intend to publish full details of these investigations in this journal. A grant from *Cellulosaindustriens forskningsstiftelse, 1959 års fond* is gratefully acknowledged.

1. Cousin, H. and Hérissé, H. *Compt. Rend.* **147** (1908) 247; *J. Pharm. et Chim.* [6] **28** (1908) 193 (*C.* **1908** II 1101); *Bull. Soc. Chim. France* [4] **3** (1908) 1070.
2. Erdtman, H. *Biochem. Z.* **258** (1933) 172; *Ann.* **503** (1933) 283.
3. Erdtman, H. *Svensk Papperstid.* **44** (1941) 243.
4. Freudenberg, K. and Richtzenhain, H. *Ann.* **552** (1942) 126.
5. Aulin-Erdtman, G. *Svensk Kem. Tidskr.* **54** (1942) 168.
6. Hergert, H. L. *J. Org. Chem.* **25** (1960) 405.
7. Naves, Y.-R. and Grampoloff, A. V. *Bull. Soc. Chim. France* **1959** 1233.

8. Leopold, B. *Acta Chem. Scand.* **4** (1950) 1531.

9. Cram, D. J. and Elhafez, F. A. A. *J. Am. Chem. Soc.* **74** (1952) 5828.

Received January 22, 1963.

Separation and Isolation of Waxes and Sterol Esters of Skin Surface Fat with Thin Layer Chromatography *

E. HAAHTI ** and T. NIKKARI

Department of Medical Chemistry, University of Turku, Turku 3, Finland

The skin surface fat consists of a mixture of hydrocarbons, sterol esters, waxes, glycerides, free fatty acids and phospholipids¹⁻³. New analytic methods, *i.e.* silicic acid chromatography and gas chromatography have elucidated the composition of the skin surface fat⁴⁻⁷. However, the separation of the waxes and sterol esters from each other has not satisfactorily succeeded with these methods⁸. The resolution of these fractions with thin layer chromatography is described in this report.

The skin surface fat was eluted with acetone from the thoracic region of the back⁶, which had been cleaned by a blank wash five hours earlier. The acetone was removed in a rotating evaporator at 50°C and the residue extracted with hexane. The hexane extract was filtered and evaporated. A sample for thin layer chromatography was taken from the dry residue and the main part was transferred on a silicic acid column to isolate a fraction containing the squalene, the waxes and the sterol esters. The details of the chromatography have been described earlier⁶. The eluate was then evaporated and the residue, 65 mg in total, was dis-

Acknowledgements * This investigation was supported by the PHS research grant H-6818 from the *National Heart Institute*, Bethesda Md., U.S.A.

** Established Investigator of the *Finnish State Medical Council*.