NOTES

Structure of Lignin

By A. B. Cramer, M. J. Hunter and Harold Hibbert

The authors have been able to isolate recently, from spruce wood, by organic solvent extraction, an aromatic ketone in high yield (about 1–2% calculated on the weight of wood taken). This ketone is an oil, distilling at a bath temperature of 140–150° (0.004 mm.). On methylation it yields a well-defined white crystalline compound, formula $C_{13}H_{18}O_4$, m. p. 81–82°. The ketone structure of the latter product was proved by its additive power for the Grignard reagent and ready formation of a hydrazone. It also contains the veratryl radical since it gives veratric acid on oxidation.

Analysis of the methylated ketone.—Calcd. for $C_{13}H_{18}O_4$: C, 65.5; H, 7.6. Found: C, 65.5; H, 7.7. Total alkoxyl found (calculated as methoxyl): 38.7%. *Grignard machine analysis:* Addition, 0.85 mole per mole weight. Active hydrogen, 0.13 mole per mole weight.

The substance from which this crystalline product apparently is derived may be one of several isomers, each consisting of a guaiacyl group with a side chain of three carbon atoms containing a carbonyl and a hydroxyl group. The syntheses of the possible methylated compounds are now in progress. The extraordinary chemical reactivity of this type of parent substance would explain the previous difficulties associated with its isolation and characterization. Such a structure provides a satisfactory basis for interpreting the results obtained in the hydrogenation of methanol lignin at high temperatures and pressures [This Journal, **60**, 1467 (1938)].

The isolated ketone is accompanied by considerable quantities of what appears to be a polymerized product, an aldehyde, an acid, a neutral substance, and a carbohydrate-containing fraction. The combined yield of all of these products calculated on the weight of the wood taken amounts to a total of 5% in the case of spruce, and roughly 10% in the case of maple.

Work now in progress on oils from hard woods indicates the additional presence of derivatives containing the syringyl group and it is possible that this may be the fundamental chemical difference between soft and hard woods.

Division of Industrial and Cellulose Chemistry
McGill University
Montreal, Canada

Received July 6, 1938

The Preparation of Amyl Salicylates

By Andrew F. Freeman and H. L. Haller

A search of the literature discloses that, of the eight theoretically possible amyl salicylates, only the normal amyl[1] and the isoamyl ester[1,2] have their properties recorded. The procedure for the preparation of the latter has been given,[2] but no reference is made to the mode of formation of the former.

In the present communication methods of preparing primary normal amyl salicylate, secondary normal amyl salicylate, and tertiary amyl salicylate are described. Isoamyl salicylate from carefully purified isoamyl alcohol and salicylic acid also has been prepared, and its physical properties have been found to be identical with those recorded by Drion.[2]

The salicylates derived from the primary amyl alcohols were prepared with sulfuric acid as the esterifying agent, but when this procedure was applied to the secondary and tertiary amyl alcohols, dehydration of the alcohol occurred, and the yield of ester was negligible. It was found, however, that the secondary and tertiary esters could be obtained on condensation of salicylic acid chloride and the carbinol in the presence of a small quantity of anhydrous aluminum chloride. With the secondary carbinol this procedure gave satisfactory yields of ester, but with the tertiary carbinol the yield of ester was small.

Primary Normal Amyl Salicylate.—A commercial grade of primary amyl alcohol was purified by fractional distillation in a column of the type described by Dupont[3] and modified by Palkin.[4] The fraction employed in the esterification had the properties: b. p. 82–83.6° at 85 mm., $n^{20}\text{D}$ 1.4109, $n^{26}\text{D}$ 1.4090, d_{20} 0.8179, $[M]\text{D}$ found 26.66, calcd. 26.815.

---

(1) "International Critical Tables," Vol. I, McGraw-Hill Book Co., Inc., New York, 1926, p. 246.

(2) C. Drion, *Compt. rend.*, **39**, 122 (1854).

(3) G. Dupont, "Les Essences de Térébenthine," Paris, 1926, p. 57.

(4) S. Palkin, *U. S. Dept. Agr.*, *Tech. Bull.*, **276** (1932); *Ind. Eng. Chem.*, *Anal. Ed.*, **3**, 377 (1931); **7**, 436 (1935).