- 2. Well-characterized derivatives of each of these types of lignin have been prepared by methylation and acylation, respectively.
- 3. Each lignin type yields a well-characterized lignin-phenol condensation product, the analysis of which shows that they are derived from a common lignin building-unit.
- 4. This building-unit, representing the *native lignin* present in spruce wood, has the empirical formula $C_{47}H_{52}O_{16}$ or $C_{42}H_{32}O_6(OH)_5(OCH_3)_5$. Of the five free hydroxyl groups at least three are aliphatic in character, while one of the remainder is of an acidic type, either phenolic or enolic. The fifth hydroxyl group differs markedly from the remaining four and is characterized by its reactivity toward alkylating reagents such as hydrochloric acid and alcohols, phenols, etc.
- 5. The phenol condensation products from Willstätter and Freudenberg lignin are shown to possess the structure $C_{42}H_{36}O_6(OH)_4(OCH_3)_5-(OC_6H_5)(C_6H_4OH)_3$.

MONTREAL, CANADA

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Note

Benzyl Levulinate

By Peter P. T. Sah, Hsing Han Lei and Hsi Meng Fang

In continuation of the studies of alkyl levulinates, 1,2 the benzyl ester has now been prepared. Of several methods tried, the following gave the best results. A mixture of 52 g. of levulinic acid, 160 g. of benzyl alcohol and 440 g. of toluene was treated with a current of dry hydrogen chloride until 7 g. was absorbed. The solution was boiled under reflux for twenty-four hours, whereupon the toluene was removed by distillation from an oil-bath at 125° and the residue fractionated under reduced pressure. A yield of about 65 g. of pure benzyl levulinate, b. p. 181–183° (17 mm.) was thus obtained. Sapon. eq. calcd. for $C_{12}H_{14}O_3$: 272.2; found 270.7. d_4^{20} 1.0935; d_4^{25} 1.0895; n_D^{20} 1.5090; n_D^{25} 1.5070.

The ester was characterized by a variety of hydrazones,3 obtained in

Hydrazone 1		M. p., °C.		Analyses, % Found Calcd.	
				Found	Calcd.
Phenyl-	Rhombic plates	91-92	N	9.46	9.73
p-Tolyl-	Rectangular plates	99-100	N	9.03	9.17
p-Chlorophenyl-	Rectangular tablets	106-107	C1	10.73	11.26
p-Bromophenyl-	Rectangular plates	103	Br	21.31	21.40

⁽¹⁾ Sah and Ma, This Journal, 52, 4880 (1930); 54, 3271 (1932).

⁽²⁾ Schuette and Cowley, ibid., 53, 3485 (1931); Cowley and Schuette, ibid., 55, 387 (1933).

⁽³⁾ Sah and Lei, Sci. Rep. Nat. Tsinghua Univ. A, 2, 1, 7 (1933).

good yields as colorless crystals, possessing sharp melting points after recrystallization from light petroleum.

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COMMUNICATIONS TO THE EDITOR

CARROT LEAF CAROTENE

Sir:

We have isolated carotene from carrot leaves to determine whether it contains the components of carrot root carotene, or whether, like the majority of leaf carotenes reported, it is optically inactive. Only two optically active leaf carotenes, tea¹ and horse chestnut,² have been reported. The method of extraction described by Smith³ was followed with minor modifications. We obtained 0.370 g. of recrystallized carotene from 6 kg. of leaf powder.

Specific optical rotations and melting points were determined on two samples, one recrystallized from petroleum ether—ethanol, the other from *n*-heptane.

Sample	(Berl block, corr.)	$[\alpha]_{6678}^{22}$		
Pet. ether-ethanol	175.7	+33.6° (36.6 mg. in 15 cc. benzene)		
n-Heptane	176.8	+37.3° (33.0 mg. in 15 cc. benzene)		

The specific rotation indicates approximately 10% of α -carotene.

The absorption spectrum in 95% ethanol was observed visually. Absorption maxima were found at 4533 Å. and approximately 4780 Å., nearly the positions of the maxima of β -carotene.

Adsorption on a column of Norit A (Pfanstiehl) from dichloromethane solution (method developed and shortly to be described by H. H. Strain) gave excellent resolution of the components. The first few drops of colored percolate, transferred to 95% ethanol, gave very sharp bands, with maxima at 4470 and 4738 Å., confirming the presence of α -carotene.

Adsorption on fibrous alumina from benzene and low boiling petroleum ether (50% by volume) showed the presence of a colored ring in the position to be expected for γ -carotene. This ring was extracted and re-adsorbed from fresh solvent on a new column. When re-extracted, the solution was too dilute for satisfactory spectroscopic identification. How-

⁽¹⁾ I. P. C. R. (Tokyo), 19, 127 (1932).

⁽²⁾ Ber., 64, 1349 (1931).

⁽³⁾ J. H. C. Smith, J. Biol. Chem., 96, 35 (1932).

⁽⁴⁾ Ber., 66, 407 (1933).