TABLE IV.—COMPETITIVE EXPERIMENTS OF ICl AND Cl_2 FOR PHENYLTRIMETHYLSILANE IN ACETIC ACID AT 25°

Concentration, 10^3M						
$[PhSiMe_3]_i$	$[Cl_2]_i$	$[ICl]_i$	$[HCl]_f$	$[PhI]_f$	Reaction, %	k_{Cl_2}/k_{ICl}
16.9	69.2	74.6	6.6	5.5	39.1	0.23
12.7	51.9	112	8.8	8.0	69.0	0.21
12.7	104	56	5.1	3.5	40.0	0.21

The response of the detector to the halobenzene and phenyltrimethylsilane was shown to be in accord with the molar concentrations of these substances by the analysis of known mixtures. Chlorobenzene was not detected among the products of the iododesilylation reaction.

Competitive Measurements.—Several competitive experiments were performed to achieve a confirmation of the greater reactivity of iodine monochloride (see ref. 8). An attempt was made to avoid the inhibition of the iododesilylation reaction by hydrogen chloride through the adoption of a short reaction time (about 100 seconds). This approach, however, was not successful. It is pertinent to recognize that a 10% increase in the amount of iodobenzene produced would yield relative rate data in good agreement with the kinetic observations. The results of three experiments are summarized in Table IV.

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The Isolation of a New Diterpene Acid

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A bicyclic diterpene acid has been isolated from the acid fraction of slash pine oleoresin (*Pinus elliotti*). This new acid, termed elliotinoic acid, was isolated by partition chromatography on a silicic acid column by the method described by Loeblich, Baldwin, and Lawrence.[2] Elliotinoic acid collected from the silicic acid column was found to be essentially pure. Several batches of slash pine oleoresin and rosin were examined and elliotinoic acid was present in all samples and was the only acid eluted in fractions 16–21. Elliotinoic acid accounts for about 5% of the acid fraction of slash pine oleoresin. The new acid resisted all efforts to crystallize it and was quite sensitive to oxidation.

Elliotinoic acid was reduced with lithium aluminum hydride to the previously reported elliotinol.[3,4] On analysis by gas–liquid chromatography, elliotinol prepared by the lithium aluminum hydride reduction of elliotinoic acid and a sample of elliotinol isolated from the neutral fraction of slash pine oleoresin were found to have the same emergence time on a silicone (SE-30) column and on mixing in equal parts only one peak was obtained. The infrared spectra, optical rotation, and melting points of the two samples of elliotinol were identical. A mixture melting point of the two samples showed no depression. The elliotinyl *p*-nitrobenzoate derivative prepared from the two samples of elliotinol had identical infrared spectra, optical rotation, and melting points, alone and when mixed.

Elliotinoic acid and elliotinol are present in about equal amounts and together account for about 10% of the slash pine oleoresin. These two compounds are the first bicyclic diterpenes isolated from the oleoresin of the slash pine.

(1) Part of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) V. M. Loeblich, *et al*, *J. Am. Chem. Soc.*, **77**, 2823 (1955).

(3) E. McC. Roberts and R. V. Lawrence, Abstracts of Papers, 131st National Meeting of the American Chemical Society, Miami, Fla., April, 1957, p. 21-O.

(4) M. Tsutsui and E. A. Tsutsui, *Chem. Rev.*, **59**, 1046 (1959).

Experimental

Isolation of Elliotinoic Acid from Rosin.—A sample containing 2.50 g. of WW slash rosin in 10 ml. of isooctane was put on a silicic acid column.[2] Fractions (100-ml.) were collected and an aliquot of each was titrated. Elliotinoic acid was eluted in fractions 16–21. These fractions were combined, washed with water, and dried. The solvent was removed under reduced pressure and the dry residue dissolved in isooctane. A sodium hydroxide solution (3 *N*) was added dropwise with constant stirring until there was no further salt precipitation. The sodium elliotinate was filtered and dried under reduced pressure. Snow white plates of sodium elliotinate (0.12 g.) were recrystallized from hot water until the melting point, ultraviolet absorption, and optical rotation were constant: m.p. 387–389° (sealed evacuated tube); $\lambda_{max}^{alcohol}$ 233 mμ (ε 27,500); $[\alpha]^{25}D$ +42° (*c* 0.5, in alcohol).

Anal. Calcd. for $C_{20}H_{29}O_2Na$: C, 74.1; H, 9.0; Na, 7.1; neut. equiv., 324. Found: C, 74.2; H, 8.9; Na, 7.0; neut. equiv., 320.

Sodium elliotinate (0.10 g.) was suspended in ether and acidified with 3 *N* phosphoric acid. The ether solution was washed neutral, dried, and the ether removed. The residue (0.08 g.) was sublimed onto a cold finger at 120° (5 μ). The sublimate was a clear colorless oil; $[\alpha]^{25}D$ +40° (*c* 1.0, in alcohol); $\lambda_{max}^{alcohol}$ 232 mμ (ε 28,900); neut. equiv., 302.

Preparation of Elliotinol from Elliotinoic Acid. A.—An ether solution containing 0.10 g. of sodium elliotinate was added slowly to an excess of lithium aluminum hydride solution. The mixture was allowed to stand overnight and water was added to destroy the excess lithium aluminum hydride. The solution was filtered and the solvent removed under reduced pressure. The oily residue was sublimed at 140° (10 μ) onto a cold finger. The alcohol crystallized in long needles on the bottom of the cold finger; m.p. 14–15°; $\lambda_{max}^{alcohol}$ 232 mμ (ε 20,600); $[\alpha]^{25}D$ +14° (*c* 2.0, in alcohol).

Anal. Calcd. for $C_{20}H_{32}O$: C, 83.3; H, 11.2. Found: C, 83.4; H, 10.9.

B.—Elliotinyl *p*-nitrobenzoate (2.30 g.), prepared from slash pine neutrals,[3] was saponified by refluxing in alcoholic potassium hydroxide. Water was added and the elliotinol extracted with ether. The ether was removed under reduced pressure to leave a yellow viscous oil (1.29 g.). A pentane solution of the oil was put through a short column of silicic acid to give 0.89 g. of a colorless viscous oil. Vacuum sublimation of this oil onto a cold finger gave pure elliotinol with infrared spectrum, optical rotation, and melting point (alone and mixture) identical with the alcohol prepared from elliotinoic acid.

Preparation of Elliotinyl *p*-Nitrobenzoate. A.—A dry pyridine (4 ml.) solution of 0.55 g. of the alcohol obtained by the lithium aluminum hydride reduction of elliotinoic acid was stirred at room temperature with *p*-nitrobenzoyl chloride for 6 hr. The resulting solution was poured over crushed ice and the water decanted. The yellow gummy precipitate crystallized from boiling 95% ethanol; m.p. 116–121°. Two crystallizations from 95% ethanol gave the pure ester; m.p. 128–130°; $[\alpha]^{25}D$ +74° (*c* 2.0 in alcohol).

Anal. Calcd. for $C_{27}H_{35}O_4N$: C, 74.1; H, 8.0. Found: C, 73.9; H, 8.0.

B.—Slash rosin neutrals (2.3 g.) in 7.0 ml. of pyridine on stirring with *p*-nitrobenzoyl chloride gave 0.63 g. of crude elliotinyl *p*-nitrobenzoate, m.p. 116–122°. Two recrystallizations from 95% ethanol gave 0.45 g. of the pure ester whose infrared spectrum, optical rotation, and melting point (alone and mixture) were identical with the ester of the alcohol prepared by the reduction of elliotinoic acid.