boiling water-bath, hydrolysis appeared to be complete within one hour. For a 2% solution of the anhydroaltroside in 0.01 *N* hydrochloric acid at 98°, the unimolecular velocity coefficient, calculated in minutes and decimal logarithms, was 0.0062; the time required for 50% hydrolysis was forty-nine minutes. Methyl α-D-glucoside in 0.1 *N* hydrochloric acid, other conditions being the same, yielded a unimolecular velocity coefficient of 0.00068; on the assumption that the rate is proportional to the acidity, this indicates that methyl 2,6-anhydro-α-D-altroside is hydrolyzed about ninety times as rapidly as methyl α-D-glucoside.

The hydrolysis of methyl 2,6-anhydro-α-D-altroside by 1 *N* hydrochloric acid at 20° was readily observed with the saccharimeter. A 4% solution required 2712 minutes for 50% hydrolysis, and the velocity coefficient was calculated to be 0.000111. An equimolecular solution of sucrose (7.8%) under the same conditions had a velocity coefficient of 0.00244 and the time required for 50% hydrolysis was 121 minutes. Hence, sucrose is hydrolyzed about 22 times as rapidly as an equimolecular solution of the anhydroaltroside.

The solutions obtained by the hydrolysis of the anhydroaltroside had a rotation, calculated as a 2,6-anhydro-D-altrose, of $[\alpha]^{20}\text{D}$ −21°. A few drops of solution restored the color to Schiff reagent within a few seconds; crystalline D-altrose restored the color slowly, and D-glucose not at all. In a separate experiment, using *N* sulfuric acid followed by neutralization with solid barium carbonate, we have been unable to obtain a crystalline 2,6-anhydroaltrose.

Hydrogenation of 2,6-Anhydro-D-altrose and the Isolation of Tetraacetyl-1,5-anhydro-D-talitol (X).—The solution obtained by the hydrolysis of several portions of methyl 2,6-anhydro-α-D-altroside (total weight 4.0 g.) with dilute hydrochloric acid were combined, neutralized to litmus with dilute sodium hydroxide, and concentrated *in vacuo* to 50 ml. The solution was transferred to the glass liner of a steel bomb, and hydrogenated, in the presence of 3 g. of Raney nickel, for six hours at 100° under a pressure of 1500 lb. per square inch. The solution no longer reduced Fehling solution. It was concentrated *in vacuo* to a dry sirup, and acetylated with 50 ml. of acetic anhydride and 50 ml. of pyridine. The acetylated product was isolated in the usual manner, and crystallized spontaneously from its concentrated ether solution. The yield was 5.5 g., or 73%. The tetraacetyl-1,5-anhydro-D-talitol thus obtained was recrystallized twice from ether, then twice from chloroform by the addition of pentane. The elongated prisms melted at 106–107°, and showed $[\alpha]^{20}\text{D}$ −16.2° in chloroform (*c*, 5); Freudenberg and Rogers[8] reported prisms of m. p. 108° and $[\alpha]^{22}\text{D}$ −15.31° in chloroform (*c*, 2).

Anal. Calcd. for $C_{14}H_{20}O_9$: C, 50.60; H, 6.07. Found: C, 50.62; H, 6.13.

The Specific Rotation of 1,5-Anhydro-D-talitol (IX).—The deacetylation of 2.4566 g. of tetraacetyl-1,5-anhydro-D-talitol by 0.5 ml. of 3% sodium methoxide in 50 ml. of methyl alcohol, followed by careful concentration of the solution in a desiccator over granular calcium chloride, yielded a sirup which in separate experiments we have been unable to crystallize. This sirup was dissolved and transferred quantitatively to a 25-ml. volumetric flask, and its rotation determined in a 4-dm. tube. Our value $[\alpha]^{20}\text{D}$ −11.4° in water (*c*, 4.85) is somewhat higher than the $[\alpha]^{23}\text{D}$ −7.34° reported by Freudenberg and Rogers for their sirup which was prepared in a different manner.

Acknowledgment.—The authors wish to thank Dr. Arthur T. Ness, Mr. Charles A. Kinser, Mrs. Betty G. Mount and Mrs. Margaret M. Ledyard of this Institute for carrying out the microchemical analyses.

Summary

Ten new crystalline derivatives of methyl α-D-altroside have been described. One of these, prepared by the action of alkali on the 6-tosyl, 6-bromo, or 6-iodo derivative, is methyl 2,6-anhydro-α-D-altropyranoside; this is a new type of anhydroglycoside, in contrast to the 3,6-anhydroglycosides of D-glucose, D-mannose, and D-galactose.

The acid hydrolysis of methyl 2,6-anhydro-α-D-altroside, followed by catalytic hydrogenation of the 2,6-anhydro-D-altrose, yields 1,5-anhydro-D-talitol; the crystalline tetraacetate of this substance has been identified with the product obtained previously by W. Freudenberg and K. F. Rogers by the catalytic hydrogenation of 2,3,4,6-tetraacetyl-2-hydroxy-D-galactal.

Bethesda, Maryland Received February 11, 1948

[Contribution from the Oregon Forest Products Laboratory and the Department of Chemistry, Oregon State College]

The Constituents of Sierra Juniper Wood (*Juniperus occidentalis*, Hooker)

By E. F. Kurth and Homer B. Lackey*

Sierra Juniper is native to altitudes ranging from 3,000 to 11,000 feet in California, Oregon, Washington, and Western Idaho. It is a low, broadheaded tree, 20 to 65 feet high, with thick trunk and stout horizontal branches. The larger trees may reach a circumference of nine feet and an age of 2,000 years. The heartwood is pale reddish-brown and the sapwood is nearly white.

It appears that no previous investigation has been made of the extractive from this species. Because large numbers of the trees are found in proposed reclamation areas, it became advisable to ascertain the constituents of the extractives from the wood.

Experimental

The material for the investigation was collected from trees felled for the purpose in the vicinity of Bend, Oregon, and included cross sections from the top and bottom of logs, stumpwood and rootwood. After the bark was removed, representative specimens of sapwood, heartwood, whole wood, stumpwood and rootwood were shredded separately in a Greundler Peerless Grinder. At the time of shredding, the moisture content of the wood was roughly 40 to 50%. For quantitative yield of extractive, samples of the shredded wood were room-dried to under 10% moisture content and then further ground in a Wiley mill to pass a 40-mesh standard U. S. sieve.

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* A part of the research reported in this paper was submitted in partial fulfillment of the requirements for degree of Master of Science in Chemistry, Oregon State College, June, 1948.

The results of extractions with ethyl ether in Pyrex glass Soxhlet extractors, and calculated on the oven-dry weight of wood, are shown in Table I. Further extraction of the ether extracted wood with acetone gave roughly an additional 1% of reddish-brown phlobaphene.

TABLE I

YIELD OF EXTRACT WITH ETHYL ETHER

Material	Per cent.
Top log	4.21
Butt log	3.36
Stumpwood	2.96
Rootwood	4.01
Sapwood	3.52
Heartwood	6.50

For the purpose of obtaining sufficient quantities of extractive to determine its chemical composition, the freshly shredded moist wood was extracted with acetone in a large metal Soxhlet-type extractor. This extractor held about 10 pounds of wood and the solvent was contained in a 45-liter, round bottom Pyrex-glass flask, which was externally steam-heated.

The acetone extracts from the wood samples were concentrated by distillation at reduced pressure in a water-bath. After the acetone had been removed, the dark colored sirupy extracts were steam distilled to remove volatile oil.

Composition of the Volatile Oil.—The aqueous condensates from the distillation with steam of the extracts from cross sections from the bole of the tree contained a crust of colorless crystals. After drying on a porous plate the crystals melted at 78° and when recrystallized from hot methanol, melted at 87°. They formed a urethan, m. p. 106–107° with phenyl isocyanate. These are the properties of cedrol, $C_{15}H_{26}O$, a tertiary alcohol occurring in few other conifers. The yield was 0.9 to 1.25% of the weight of the wood.

The volatile oils from the stumpwood and rootwood were nearly colorless liquids from which crystals did not separate. They were removed from the aqueous layer by shaking out with petroleum ether in a separatory funnel.

Thirty-five grams of the oil from the rootwood extract was distilled at a pressure of 9 mm. from a 60-ml. round-bottomed flask heated in an oil-bath. Twenty-eight grams of a clear colorless oil distilled between 130 to 170°. A dark brown residue, presumably decomposition and polymerization products, remained. The oil was fractionally distilled at 41 mm. into two distinct fractions. The first fraction, a clear colorless oil amounting to 49.3% of the original rootwood oil, was identified as cedrene, $C_{15}H_{24}$. It had the following properties: b. p., 131–133° (18 mm.), 264° (759.8 mm.); sp. gr. 0.9322 $^{20}/_{20}$; sp. rotation, $[\alpha]^{20}_{D}$ in chloroform $-58°\ 5'$; refractive index, $1.5008^{20°}$. A dilute solution in 95% ethanol gave an immediate reddish color which changed to red-violet upon the addition of a solution of one-tenth g. of vanillin dissolved in 100 ml. of concentrated hydrochloric acid.

The second fraction was the white crystalline solid cedrol, $C_{15}H_{26}O$. It distilled between 155 to 165° at 41 mm., melted at 86°, and had a specific rotation, $[\alpha]^{20}_{D}$ $+8°\ 29'$. The urethan from phenyl isocyanate melted at 106–107°. The cedrol crystals when dissolved in absolute ethanol and dehydrated with concentrated phosphoric acid gave cedrene, which gave the typical color with the vanillin–hydrochloric acid reagent.

Separation of Phlobaphene.—The thick, dark-colored residues from the separation of the volatile oil were placed in a separatory funnel and shaken with successive portions of ethyl ether. The insoluble material was then refluxed for an hour with more ether, whereupon a reddish-brown residue was obtained that dried to an amorphous powder.

This material gave a green-black coloration with dilute solutions of iron salts, precipitated gelatin from solution, and upon methylation with dimethyl sulfate in alkaline solution followed by oxidation with potassium permanganate gave veratric acid, m. p. 177°, methyl ester m. p. 55–57°. The dried product was only slightly soluble in water. This indicated that a catechol phlobaphene is present in Sierra juniper wood. The yield was roughly 1% of the weight of the whole wood.

Separation of Petroleum Ether Solubles.—The ether solutions from the separation of the phlobaphene were washed with water, dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The dark colored resinous material was then extracted with petroleum ether. This solvent extracted a reddish yellow product and gave a dark colored resinous precipitate.

The petroleum ether solutions were next shaken in a separatory funnel with successive portions of 5% potassium carbonate solution to separate acidic substances from neutral materials. Complete separation of the sapwood extract, as judged by the color of the aqueous layer, was comparatively sharp after shaking with four portions of potassium carbonate solution. The coloring matter was more difficult to remove with the other wood extracts, which required up to 9 extractions with fresh portions of potassium carbonate solution. The petroleum ether solutions were then washed with water and dried over anhydrous sodium sulfate overnight. The ether was removed under reduced pressure and the residues weighed. The amounts of neutrals and acids found, as well as those of other components, are given in Table II. The method of separation is summarized in Fig. 1.

TABLE II

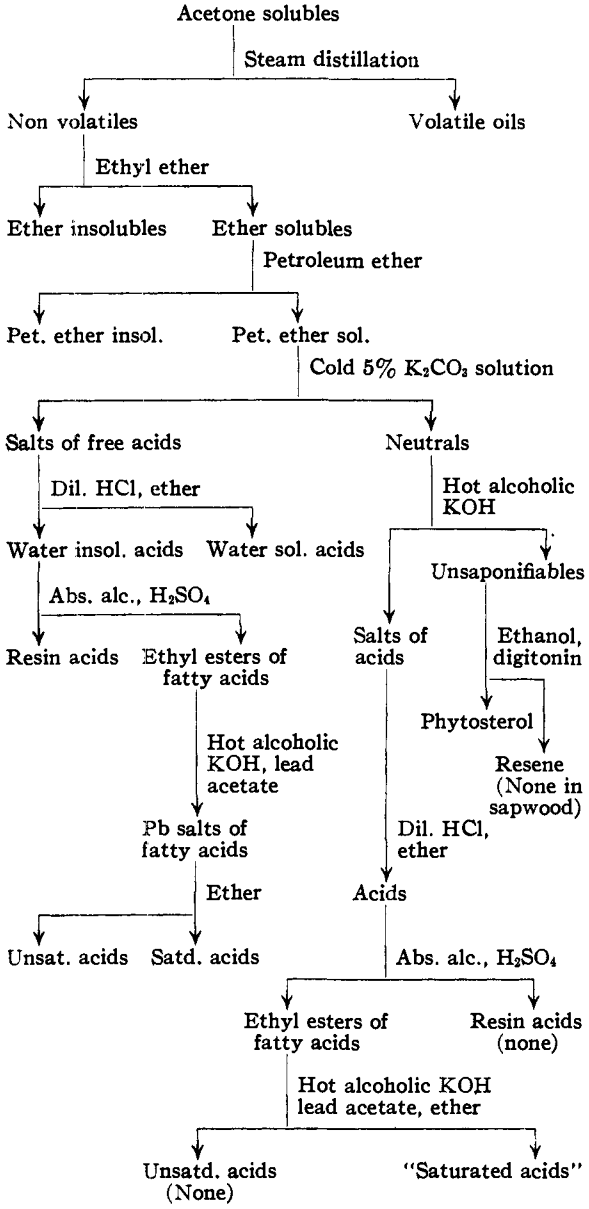
COMPOSITION OF PETROLEUM ETHER EXTRACT FROM SIERRA JUNIPER (YIELD FROM SAPWOOD 2.53%; FROM WHOLE WOOD 3.01%)

	Per cent. of total pet. ether extract	
	Sapwood	Whole wood
Free acids	27.9	43.6
Fatty acids	21.6	26.4
Resin acids	6.3	17.3
Combined acids	27.1	6.9
Fatty acids	27.1	6.9
Resin acids	0.0	0.0
Total acids	55.0	50.5
Saturated fatty acids	30.9	14.6
Unsaturated fatty acids	17.7	16.0
Resin acids	6.3	17.3
Unsaponifiables	45.0	49.5
Volatile oils		1.0
Phytosterol	45.0	5.0
Resene		43.5
Water solubles	None	Trace

Esterification of the dry acidic fractions with ethanol and sulfuric acid gave a separation into fatty acids and resin acids. The resin acid fraction from all of the wood extracts was dark colored and non-crystallizable from a variety of solvents. The neutral equivalent varied from 297 to 337, whereas that for abietic acid is 302.4.

The fatty acid fractions were further separated into presumably saturated and unsaturated acids by the difference in solubilities of their lead salts in ether. The unsaturated fatty acids thus obtained were red colored liquids, which gave iodine numbers by the Hanus method ranging from 56.7 to 68.1 and neutralization equivalents ranging from 338 to 346. This indicated that acids with more than 18 carbon atoms were present. Oxidation with cold alkaline potassium permanganate resulted in the isolation of dihydroxystearic acid, m. p. 129.5°, which indicated that oleic acid was present in the mixture.

Fig. 1.—Separation of the juniper wood extract



The saturated fatty fraction was soluble in warm methanol and crystallized from this solvent on standing. After several recrystallizations, white waxy solids were obtained, which melted at 72.5–73°. Decomposition took place at temperatures above 100°, which demonstrated a relative low stability to heat. The crystals were soluble in warm dilute sodium hydroxide, but were insoluble in 5% sodium bicarbonate solution. Neutralization values of 677 to 684 were obtained. Other investigators have obtained similar acids from Jack pine and Swedish Tall oil[1,2,3] and considered them lactonic acids.

After refluxing the crystals for one-half hour with an excess of alcoholic potassium hydroxide, acidifying the solution, extracting with ether, drying and recrystallizing, the neutral equivalent was lowered to between 396 to 422. This indicates that the material could be the dibasic lactonic acid of the same melting point described by Sandquist.[3]

The neutral fractions were saponified with 7% alcoholic potassium hydroxide by the modified Kerr–Sarber method of Jamieson[4] and separated into unsaponifiable matter and acids. No resin acids or ether soluble lead salts were found present in the acid fraction. The only acid isolated had the same properties as that described in the preceding paragraphs.

Unsaponifiables.—A one per cent. solution of the unsaponifiables in absolute ethanol was heated and to it was added an equal volume of a 1% solution of digitonin in 95% ethanol. After standing in a refrigerator for forty-eight hours, white crystals of phytosterol digitonide separated. The yield of digitonide was quantitative from the sapwood unsaponifiable matter inasmuch as no residue was found in the filtrate. The unsaponifiable from the whole wood contained only approximately 10% of sterols. The bulk of the unsaponifiable matter from this extract was not precipitated by digitonin.

The phytosterol was recovered from the unsaponifiable matter by crystallization from hot dilute alcohol. The light colored crystals, which separated, were decolorized with charcoal, and recrystallized successively from hot dilute ethanol and acetone. The properties are shown in Table III. From the experimental data in this table, the product appears to be a mixture of *alpha* and *beta* sitosterol.

TABLE III

PROPERTIES OF THE PHYTOSTEROL

	Sierra juniper wood	α-Sitosterol[4]	β-Sitosterol[4]
Melting point, °C.	134–136.5	135–136	139–140
Melting point of acetate, °C.	125.5–128		127–128
Specific rotation $[\alpha]^{20}_D$ in $CHCl_3$	−21.25	−13.45	−36.11

The filtrate from the precipitation of the phytosterol digitonide from the whole wood unsaponifiables was concentrated and diluted with water, whereupon a resene was precipitated. This was recrystallized successively from hot dilute ethanol, methanol and acetone and had a melting point of 76–78.5°. It was slightly soluble in hot water and very soluble in petroleum or ethyl ether, benzene and chloroform. The compound was optically inactive. Molecular weight, as found by the Rast camphor method, together with carbon and hydrogen analyses indicated the empirical formula to be $C_{18}H_{31}O$.

Calcd. for $C_{18}H_{31}O$: C, 82.10; H, 11.86; molecular weight, 263.4. Found: C, 81.72; H, 12.10; molecular weight 262.0.

An acetate was formed by refluxing the resene for one-half hour with acetic anhydride and anhydrous sodium acetate. It had a melting point of 102–104°. Formation of the acetate established the resene as an alcohol.

Petroleum Ether Insoluble Fraction.—Investigation of this fraction gave many variable results. It appeared to be in various stages of oxidation and polymerization. In addition to being soluble in ethyl ether it was soluble in ethyl acetate, partly soluble in hot methanol and hot benzene. The product from the top log cross section, amounting to 46.2% of the ethyl ether extract, upon saponification with sodium hydroxide gave an insoluble sodium salt. The material soluble in sodium hydroxide was a mixture of resin and fatty acids. Decomposition of the insoluble sodium salt with dilute acid precipitated a light brown granular solid with a neutral equivalent of 791.

The product from a cross section of a butt log with some dry rot at the core gave on redissolving in ethyl ether and upon slow evaporation of the solvent, light fluffy crystals.

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(1) H. Hibbert and J. B. Phillips, *Can. J. Research*, **4**, 1 (1931).

(2) T. Hasselstroem, *Paper Trade J.*, **83**, No. 2, 66 (1926).

(3) H. Sandquist, *Z. Angew. Chem.*, **35**, 531 (1922).

(4) Jamieson, George S., "Vegetable Fats and Oils," A. C. S. Monograph No. 58, 2nd ed., Reinhold Publishing Corp., New York, N. Y., 1943.

These were recrystallized from hot benzene and then had the following properties: insoluble in water, petroleum ether and carbon tetrachloride; slightly soluble in ethyl ether, benzene, and ethyl acetate; and soluble in alcohol, acetone, and sodium bicarbonate solution; m. p. 229°, neutral equivalent 153, molecular weight 294, C 60.8%, and H 7.42%. This indicated an empirical formula of $C_{15}H_{22}O_6$. Methoxl groups were absent.

The compound formed a mono methyl ester with methanol in the presence of concentrated sulfuric acid that had the following properties: m. p. 136–137°, neutral equivalent 290, saponification equivalent 164. The ester was soluble in sodium bicarbonate solution and after saponification the original compound was recovered. These properties indicated a dibasic acid.

The compound was obtained in only small yield from one specimen of Sierra juniper wood containing dry rot.

Inasmuch as it was not isolated from sound wood it is questionable whether it is a normal constituent of wood with no decay.

Summary

1. The ethyl ether soluble content of Sierra juniper wood was found to range between 2.96 to 6.5%. Approximately an additional one per cent. of material is soluble in acetone which is chiefly a catechol phlobaphene. A part of the ethyl ether extractive is soluble in petroleum ether. This amounted to 2.53% on the weight of sapwood and 3.01% on the weight of the whole wood from a cross section of the trunk. A detailed analysis of the petroleum ether solubles is tabulated.

2. The constituents of the petroleum ether extract were resin acids, oleic acid and high molecular weight lactonic acids, a mixture of alpha and beta sitosterol and a hydroxy resene, $C_{18}H_{31}O$. The resin acids occurred only in the free state.

3. The volatile oil from the trunk of the tree ranged from 0.9 to 1.25% and was apparently entirely cedrol. That from the rootwood was a mixture of cedrene and cedrol.

CORVALLIS, OREGON RECEIVED MARCH 16, 1948

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Jacobsen Reaction. IX.[1] 6,7-Dialkyltetralins

BY LEE IRVIN SMITH AND CHIEN-PEN LO[2]

The only tetraalkylbenzenes so far studied with reference to their behavior under the conditions of the Jacobsen rearrangement are those in which the alkyl groups are methyl and ethyl. Tetraalkylbenzenes of known structure, having alkyl groups above ethyl, and with straight or branched chains, are practically unknown, and the variety and number of such compounds necessary for an extended study of the Jacobsen reaction make the preparation of the starting materials and reference compounds a very formidable task. In the previous paper[1] it was shown that a cyclic chain attached at two ortho-positions to a benzene ring could take the place of two alkyl groups in a tetraalkylbenzene, and it was shown that 6,7-diethyltetralin (a 1,2,4,5-tetraalkylbenzene) underwent the Jacobsen reaction in the normal fashion to produce 5,6-diethyltetralin (a 1,2,3,4-tetraalkylbenzene). Indeed, Schroeter and Gotzky[3] had already shown that two cyclic chains, involving the 1,2,4,5-positions of a benzene ring could replace four alkyl groups, for these authors observed that octahydroanthracene, subjected to the conditions of the Jacobsen reaction, underwent rearrangement to octahydrophrenanthrene, a 1,2,3,4-tetrasubstituted benzene. 6,7-Dialkyltetralins are quite readily prepared in some variety; moreover, these substances, as well as their rearrangement products, are readily dehydrogenated to the corresponding naphthalenes, so that the problems of identification can be solved without much difficulty.

Arnold and Barnes[1] have recently proposed a theory for the mechanism of the Jacobsen reaction. According to this theory, the migrating alkyl group is detached from the sulfonic acid molecule as a cation; this cation then replaces the more hindered sulfonic acid group of the (di)-sulfonic acid, leading to the rearranged sulfonic acid. As a necessary consequence of this theory, migration of a *n*-propyl group in a polyalkylbenzene would involve simultaneous isomerization of the group to iso-propyl, since the latter is the more stable of the two propyl cations under the conditions of the rearrangement.

With the objectives of testing this corollary of the suggested mechanism, and of extending the data on the Jacobsen reaction to groups other than methyl and ethyl, five (four of them new compounds) 6,7-dialkyltetralins have been prepared and subjected to the conditions of the Jacobsen rearrangement. Each tetralin was dehydrogenated to the corresponding naphthalene and the latter identified—hence, incidental to this work, a number of new 2,3- and 1,2-dialkylnaphthalenes have been prepared and characterized.

I, R = R′ = CH_3
II, R = CH_3, R′ = *n*-C_3H_7
III, R = CH_3, R′ = iso-C_3H_7
IV, R = C_2H_5, R′ = iso-C_3H_7
V, R = R′ = *n*-C_3H_7

When 6,7-dimethyltetralin (I) was subjected to the conditions of the Jacobsen reaction, it was converted into 5,6-dimethyltetralin, in analogy

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[1] No. VIII, Arnold and Barens, THIS JOURNAL, **66**, 960 (1944).

[2] Abstracted from a thesis by Chien-Pen Lo, presented to the Graduate Faculty of the University of Minnesota, in partial fulfillment of the requirements for the Ph.D. degree, September, 1947.

[3] Schroeter and Gotzky, *Ber.*, **60**, 2035 (1927).