[Contribution from the Department of Chemistry, University of Toronto]

The Oxymercuration of Δ^1-Terpineol*

A. G. BROOK AND GEORGE F WRIGHT

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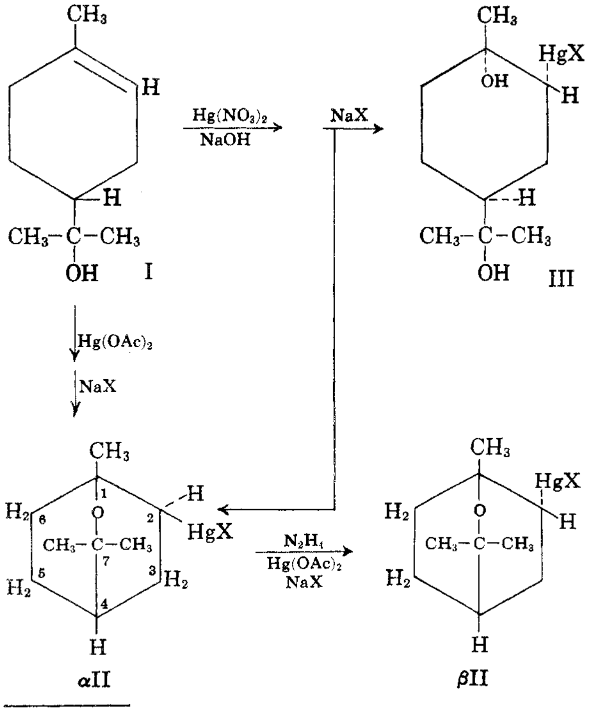
The supposed diastereomers of 2-iodomercuri-*trans*-terpin reported by Sand and Singer have been found to be polymorphs. It has also been shown that the *trans*-terpin mercurial is not an intermediate in the formation of the halogenomercuricineoles, which seem to be formed directly from the salt expected from the alcoholysis of mercuric acetate by Δ^1-terpineol. It has been found that hydrogen sulfide decomposes α-halogenomercuri-*trans*-terpin to give terpineol, whereas comparable treatment of the β-diastereomer yields bis(*trans*-terpinmercuri) sulfide. The β-diastereomers of the halogenomercuricineoles have been prepared by equilibration with the α form by hydrazine hydrate. The unusual stability of these β-diasteromers toward hydrochloric acid lends support to the theory that decomposition of oxymercurials by this acid proceeds through a quasi-cyclic intermediate. There is still doubt whether addition of the elements of mercuric salts to alkenes occurs in the *cis* or *trans* manner despite the fact that this reaction has been known for more than fifty years. This doubt has not been dispelled in the present study of Δ^1-terpineol oxymercuration. However a choice must be made in order to describe the terpins and cineoles which have been prepared. We have chosen to express the stereochemical structures in terms of *cis* addition and elimination because this expression describes best the known facts of oxymercuration, whereas *trans* addition and elimination may at present be applied only by analogy with reactions which are not necessarily related to oxymercuration. If new facts of oxymercuration subsequently favor the *trans* mode then the terpin structures of section I and the cineole structures of section II may easily be revised in accordance with such new discoveries.

I. TERPIN MERCURIALS

It has recently been shown[1] that the two pairs of compounds which Sand and Singer[2,3] reported as the oxymercuration products of 2,6-dimethylhepten-5-ol-2 were in reality one cyclic and one linear oxymercurial. In the same publications Sand and Singer described the oxymercuration of Δ^1-terpineol (I). They reported that one bicyclic and two monocyclic oxymercurials were obtained when the basic reaction mixture was treated with sodium iodide and carbon dioxide.



They specified that the bicyclic compound, to be discussed in Section II, was 2-iodomercuri-1,8-cineole (II, X = I) because they were able to reduce it with sodium amalgam to 1,8-cineole. We have confirmed their opinion, first by reduction with hydrazine hydrate[4] to give cineole, and second by oxidation of II with alkaline permaganate to yield cineolic acid. They also reduced their monocyclic products to *trans*-terpin by means of sodium amalgam, and this designated the mercurials as 2-iodomercuri-*trans*-terpins (III, X = I). Since oxygen was thus shown to be attached to carbon 1 in all three products, the isomeric forms of III seemed not to be position isomers. Sand and Singer then designated III (X = I) in two diastereomeric forms. Since both products, upon reduction, yielded *trans*-terpin, it is evident that their postulated diastereoisomerism must involve the disposition of the hydroxy versus the iodomercuri group.

This designation may be questioned from two aspects. First, no instance is yet known when a single geoisomer (in which category Δ^1-terpineol must be considered) has yielded more than a single diastereomeric mercurial. Second, Sand and Singer reported that the low-melting form of III was converted to the high-melting form simply by treating with cold absolute ethanol or by heating in benzene or ethyl acetate. Such easy conversion is not characteristic of diastereomers. However Sand and Singer also reported that the low-melting form of III was more easily hydrolyzed by aqueous acids than was the other. This property has been found to be characteristic of diastereomeric oxymercurials.[4-6]

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* This paper is a contribution in honor of Lyndon F. Small, former Editor of the Journal.

(1) A. G. Brook, A. Rodgman, and G. F Wright, *J. Org. Chem.*, **17**, 988 (1952).

(2) J. Sand and F. Singer, *Ber.*, **35**, 3170 (1902).

(3) J. Sand and F. Singer, *Ann.*, **329**, 166 (1903).

(4) G. F Wright, *Can. J. Chem.*, **30**, 268 (1952).

(5) J. Romeyn and G. F Wright, *J. Am. Chem. Soc.*, **69**, 697 (1947).

(6) A. G. Brook, R. Donovan, and G. F Wright, *Can. J. Chem.*, **31**, 536 (1953).

It thus seemed worthwhile to resolve this discrepancy by repetition of the work of Sand and Singer.

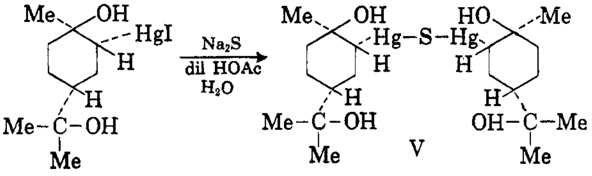
We found at once that the low-melting form of III (X = Iodine) is not so stable as Sand and Singer implied. When first isolated, it is a gummy solid at 25°, although it is hard and brittle at 4°. Its melting point gradually rises from 45–50° to 91° over a period of four days at 25°. When either high-melting (m.p. 143–4° after crystallization from benzene) or the unstable low-melting isomer is dissolved in alkali and reprecipitated by carbon dioxide, it cannot be predicted which isomer will be obtained. However, deliberate inoculation with one of the isomers at the moment before precipitation when the liquor becomes cloudy always promotes precipitation of that isomer. This behavior designates the isomers as simple polymorphs.

The physical and chemical properties of the two isomers of III (X = Iodine) are those usually expected for labile and stable polymorphic modifications. The low-melting (labile) modification dissolves more easily in a variety of solvents than the high-melting form. Each shows a characteristic X-ray diffraction powder pattern, although the pattern of the labile polymorph obviously is less distinctive than that of the stable form, which can be crystallized to high purity. The polymorphism of 2-iodomercuri-*trans*-terpin may extend to the chloromercuri analog (III, X = Cl). But when either of the polymorphs of III (X = Iodine) is treated with silver acetate and then with sodium chloride only one chloromercuri-*trans*-terpin is obtained. This would seem to constitute sufficient proof that III (X = I) exists in polymorphic rather than diastereomeric form. There is, then, not yet an exception to the rule that in oxymercuration the addition to an alkene linkage is diastereomerically unique.

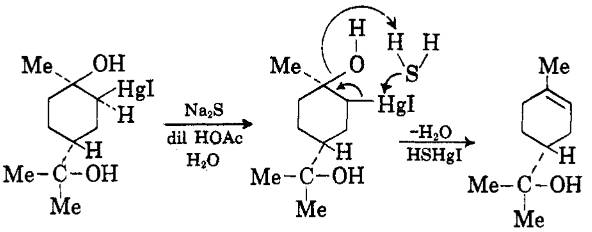
The single diastereomer (III) is evidently 2-halogenomercuri-*trans*-terpin, notwithstanding the fact that the structure proof involving reduction with sodium amalgam is not completely reliable. Such a reducing agent has been known to remove the oxymercurial addend with regeneration of the alkene linkage. However if such a reaction sequence had occurred in the present instance (and water had then added to the double bond), the product would have been *cis*-terpin hydrate. The latter geoisomer is invariably the product when Δ^1-terpineol is hydrated.[7] Since only *trans*-terpin was isolated after reduction with sodium amalgam, the hydroxyl group in III must be situated oppositely from the hydroxypropyl group with respect to the cyclohexane ring. It will be assumed subject to further consideration that the mercuri substituent is oppositely disposed relative to the hydroxypropyl group.

Since the 2-iodomercuri-*trans*-terpins of Sand and Singer are polymorphs rather than diastereomers we suggest that their designations, "alpha" and "beta," be abandoned in favor of "labile" and "stable" forms. The Greek letters may then be used according to an earlier suggestion[4] to designate the diastereomer obtained from a *cis*-alkene as "alpha," and from a *trans*-alkene as "beta." Since Δ^1-terpineol resembles cyclohexene in its geometry the pair of polymorphs (III, X = Iodine) may be said to comprise the α-diastereomer of 2-iodomercuri-*trans*-terpin.

The α-diastereomer may be converted to a mixture of itself and the β form of III (X = Iodine) by treatment of a hot alkaline solution of α-III with a small amount of hydrazine hydrate.[4] When this mixture is treated carefully with hydriodic acid, the α part is decomposed to Δ^1-terpineol and mercuric iodide. After the system is made basic and steam-distilled to remove terpineol, the β-diastereomer may be isolated by acidification. Reduction of this more stable isomer by sodium amalgam yields *trans*-terpin, showing that the configuration of the mercuri group, but not the hydroxy group, has been inverted relative to the hydroxypropyl group in the β-diastereomer.



β III



α III IV

In accordance with previous observations[6] the dipole moment of β-iodomercuri-*trans*-terpin (4.59 D) in dioxane solution at 20° is found to be larger than the comparably-determined moment (4.21 D) of the α-diastereomer. This difference may be related to the behavior of the two diastereomers towards sodium sulfide. The α-diastereomer (α-III, X = I) reacts quickly in aqueous acetic acid with regeneration of terpineol, I. We suggest that this demercuration occurs *via* a cyclic intermediate (IV) in which molecular hydrogen sulfide partakes. By contrast β-III (X = I) reacts with sodium sulfide to give β-bis(*trans*-terpinmercuri) sulfide (V). The stability of this sulfide, unique among comparable oxymercurials so far investigated, may be attributed to steric reactions not present in the demercuration of the β-diastereomer. Such steric

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(7) J. L. Simonsen, *The Terpenes*, Cambridge Press, 1947, Vol. 1, p. 302.

effects would be operative in the cyclic intermediate which we have postulated.

II. THE CINEOLE MERCURIALS

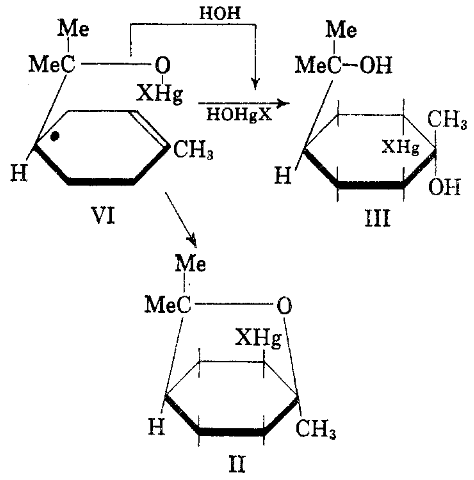
One can not discern from the reaction procedure of Sand and Singer whether the bicyclic cineolmercurial (II) is formed directly from Δ^1-terpineol or indirectly from a mercurial of *cis*- or *trans*-terpin by spontaneous dehydration. One might postulate that the theoretically-possible nitratomercuri-*cis*-terpin was indeed formed by *cis* oxymercuration but subsequently lost the elements of water to form nitratomercuricineole.[2,3] Alternatively the diastereomeric nitratomercuricineole might have been formed from nitratomercuri-*trans*-terpin *via* replacement of hydroxyl by tertiary alkoxyl at C_1 with inversion.

The effect of *p*H during the hydroxymercuration of α-terpineol has been shown by Mr. Paul Chu to vitiate the first alternative.

The *p*H of the basic mercuric salt as described by Sand and Singer[2,3] lies between 1 and 2. In this system the yields of α-2-iodomercuri-*trans*-terpin and α-2-iodomercuricineole were 62% and 8% respectively. If the *p*H were raised to 3, where some mercuric oxide appeared, the yields were 56% and 25%. When sodium acetate as a buffer raised the *p*H to 4–5 the yields were 40% and 37% respectively while at *p*H 6 they were 24% and 39%. Thus it may be seen that the 2-iodomercuricineole yield is highest under conditions where ether formation by dehydration ought to be least. Actually the yield of the bicyclic product is greatest in circumstances where the *tert*-alkoxymercuric salt (see VI, X = OAc) ought to be most stable.

Indeed it is found that mercurated cineole is formed under conditions where the mercurated terpin cannot be present. By treatment of anhydrous Δ^1-terpineol with mercuric acetate in suspension we have shown that αII (X = OAc) can be formed directly. Some oxidation occurs at the same time since 15% of the mercuric salt is reduced to the mercurous form. The oxidation product (identified by Mr. D. A. Shearer of this laboratory as pinol hydrate, 6% yield) is separable from the mercurial because of its insolubility in alkali. The separated alkaline solution precipitates a 60% yield of α-2-chloromercuricineole when it is treated with sodium chloride and carbon dioxide.

The mechanism by which the cineole mercurial (II) is formed may be illustrated by postulation of the basic mercuric salt (VI, X = OAc) as an intermediate. In absence of water, II can be the only mercurial formed, but when water is present this intermediate may be expected to hydrolyze either before or after hydroxymercuric acetate has been added to the double bond to form the *trans*-terpin mercurial (III, X = OAc). In the latter event the presence of the hydroxypropyl group or its mercuric salt would be expected on steric grounds to prevent formation of the diastereomer alternative to III which could be formed by *cis* addition.



The reduction of an alkaline solution of 2-iodomercuricineole by an excess of hydrazine hydrate was shown in the present report to yield cineole. On the other hand a stoichiometric deficiency of hydrazine hydrate forms a diastereomeric mixture of α- and β-iodomercuricineoles; the same behavior is observed with the α-bromo- and α-chloromercuricineoles. β-Chloromercuricineole may be isolated from the diastereomeric mixture because of its stability (unique among any vicinally-linked oxymercurials that are known) toward mineral acid. This property is undoubtedly related to the rigidity imposed by the bicyclic ring system. The stability of the β-isomer is utilized for its isolation by dissolving the mixture in alkali and then acidifying with hydrochloric acid.[5] The α-diastereomer is immediately decomposed to Δ^1-terpineol and mercuric chloride. The terpineol may be removed by steam distillation of the suspension after it is made basic. The residual liquor is filtered to remove mercuric and mercurous oxides, then acidified with hydrochloric acid to precipitate the β-chloromercuricineole. The β-bromo- and β-iodomercurials are obtained by appropriate modifications.

The β-halogenomercuricineoles differ from their α-diastereomers not only in stability toward mineral acid but also in lower melting points and greater solubility in hydroxylic solvents. On the other hand β-hydroxymercuricineole is much less soluble in hydroxylic solvents than the α-diastereomer, and this property may also be utilized in separation of the two.

The electrical polarizations of the α and β chloromercuricineoles have been determined in dioxane at 20° as 314.8 and 556.8 cc. respectively by calculation from the dielectric constants and specific volumes of the solutions according to the method of Halverstadt and Kumler.[8] From the di-

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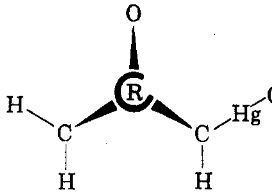
(8) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

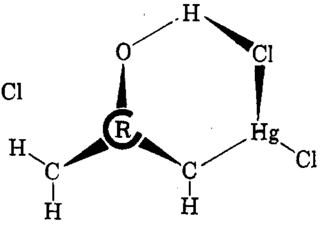
electric constants of a series of pellets[9,10] the combined atomic and electronic polarization has been found to be 68.5 cc. for the α- and 66.9 cc. for the β-diastereomer. From these data the dipole moment is calculated as 3.42 D for α-chloromercuricineole and 4.82 D for the β-diastereomer. Thus the cineole mercurials resemble other diastereomeric pairs of oxymercurials since the form having the lowest dipole moment is the one most easily decomposed by mineral acids.[4-6]

The group fixation in these cineoles permits of comparison with the oxy- and mercuri-groups which are fixed analogously in the oxymercuration product of 1,4-↑↑-methylene-Δ^5-cyclohexene-2,3-↓↓-dicarboxylic acid.[11] In both instances the bridge limits the variety of atomic constellations that are otherwise possible in a cyclohexane ring system. Insofar as 5-↓-hydroxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2,3-dicarboxylic acid, γ lactone of moment 3.88 D and its inverted diastereomer 5-↓-hydroxy-6-↑-chloromercuri-1,4-↑↑-methylenecyclohexane-2,3-dicarboxylic acid, γ-lactone of moment 7.18 D[12] can be compared with the α- and β-chloromercuricineoles a configurational assignment may be made. According to this criterion the α-diastereomer would be represented by the plan and side elevations shown as structures VII and VIII (R = CH_3) while the β-diastereomer would be represented, in plan elevation, as IX.

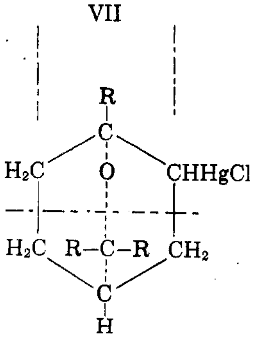
Other opinions in respect of the mode of addition in oxymercuration have been expressed.[13] Those favoring "trans" addition would describe the bicyclic oxymercuration product of Δ^1-terpineol as IX. A final decision should not be made on the basis of the evidence now available. However it may be noted that the planar arrangement of O-C-C-HgCl in IX should from conformational considerations be unusually favorable for demercuration if such elimination occurred in the *trans* manner. Actually α-2-chloromercuricineole is not unduly sensitive toward acid-actuated demercuration. Moreover highly dissociated acids are not very effective, and demercuration occurs easily only when hydrogen halides are present in molecular form. This behavior has led us to favor structure VII-VIII as the α-diastereomer because it permits the existence of a quasi-cyclic complex (X) with hydrogen halide. If easy demercuration involves such a complex, it is understandable that β-chloromercuricineole, if it is represented by IX, is very resistant to the action of hydrogen halide.



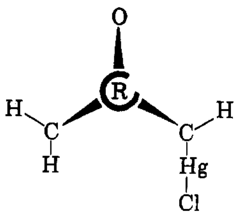
VII



X



VIII



IX

EXPERIMENTAL[14]

α-2-Chloromercuricineole. A. From mercuric acetate. A suspension of 160 g. (0.5 mole) of mercuric acetate in 375 g. (2.42 mole) of Δ^1-terpineol was stirred at 40–45° for 2 days (although a test for mercuric ion was negative after 12 hr.) and then was filtered by suction to remove 26.4 g. of mercurous salt. From the filtrate was distilled 228 g. of unchanged Δ^1-terpineol at 60–70° under 0.01–0.001 mm. The residue was suspended in 200 ml. of petroleum ether (b.p. 60–70°). This suspension was extracted successively with 400, 300, and 200 ml. of 5% aqueous sodium hydroxide and then with four 200 ml. portions of water. The combined aqueous extract was treated with Darco decolorizing charcoal and filtered. After solution of 100 g. of sodium chloride into this filtrate, it was saturated with carbon dioxide. The vacuum-dried precipitate weighed 122 g., m.p. 151°. This was crystallized from 1400 ml. of hot 95% ethanol with 1 g. of Darco. The purified product weighed 83 g. (43%) and melted at 164°. The X-ray powder diagram gave relative intensities at d spacings of [10] 16.05; [9] 10.71; [7] 5.30; [6] 3.22; [4] 7.96, 2.65; [3] 5.88, 4.39, 3.77, 3.65, 2.86; [2] 5.62, 4.91, 3.96, 3.57, 3.42, 2.45, 2.16; [1] 4.61, 2.77, 2.10.

Anal. Calcd. for $C_{10}H_{17}OHgCl$: C, 30.9; H, 4.37. Found: C, 30.7; H, 4.39.

The petroleum ether extract, when combined with the evaporated mother liquors from crystallization was steam-distilled with 10% alkali to remove residual Δ^1-terpineol. The non-aqueous residue was crystallized from chloroform, which yielded 5.1 g. (6%) of impure pinol hydrate. After crystallization from chloroform and benzene it melted at 133.0–133.5°. A mixed melting point with an authentic specimen was not lowered.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.6; H, 10.6. Found: C, 70.0; H, 10.8.

B. From basic mercuric nitrate in water. A solution of mercuric nitrate was prepared from 21.6 g. (0.1 mole) of mercuric oxide in 80 ml. of 20% nitric acid. A solution of 15.4 g. (0.1 mole) of Δ^1-terpineol (d_4^{28} 0.936, n_D^{20} 1.47902) in 30 ml. of diethyl ether also was prepared. To the first solution in a separatory funnel was added 10% aqueous potassium hydroxide until a white precipitate appeared. A portion of the second solution was added and the mixture was shaken while the ether was allowed to boil away through the stop cock. Alternate addition of alkali to restore the white pre-

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[9] C. C. Meredith and G. F Wright, *Can. J. Technology*, **33**, 182 (1955).

[10] C. C. Meredith, L. Westland, and G. F Wright, *J. Am. Chem. Soc.*, **79**, 2385 (1957).

[11] K. H. McNeely, A. Rodgman, and G. F Wright, *J. Org. Chem.*, **20**, 714 (1955).

[12] G. F Wright, *Annals New York Academy of Science*, **65**, 436 (1957).

[13] J. Chatt, *Chem. Revs.*, **48**, 7 (1951).

[14] All melting points have been corrected against reliable standards. X-Ray diffraction patterns were determined with CuK_α radiation (Ni filtered) and are recorded as d spacings in Å at relative intensities $[I/I_0]$.

cipitate and of terpineol to remove it until final addition of alkali (about 250 ml. total) precipitated black mercurous salt. The mixture was filtered and the filtrate treated with 15 g. of potassium hydroxide dissolved in 30 ml. of water. To this slightly cloudy solution was then added 15 g. (0.09 mole) of potassium iodide in 20 ml. of water. The precipitate was filtered off. This 3.80 g. yield (8%) of 2-iodomercuricineole was crystallized from 50 ml. of absolute ethanol, m.p. 151–152°. Its X-ray diffraction pattern was [10] 5.98, 3.45; [8] 12.62; [6] 11.32, 7.49; [5] 3.16, 1.84, 1.57; [4] 5.21, 4.48, 2.96, 2.44, 2.23, 1.99, 1.93; [3] 3.61, 2.56, 2.34, 2.14; [2] 4.72, 4.23, 4.00, 1.68; [1] 2.81, 1.86, 1.79, 1.73, 1.65, 1.60, 1.55, 1.52, 1.48, 1.44, 1.42, 1.39, 1.35, 1.27, 1.18, 1.14, 1.11, 1.08, 1.04, 1.00, 0.97.

This product could be converted to 2-chloromercuricineole in 65% yield by treatment of 0.6 g. (0.00125 mole) and 0.26 g. (0.0016 mole) of silver acetate as a suspension in 7 ml. of ethanol and 8 ml. of water for 12 hr. The silver halide was then filtered off. The filtrate was treated with 15 ml. of potassium hydroxide to remove mercurous salt. The alkaline filtrate was treated with 10 ml. of saturated aqueous sodium chloride and then with gaseous carbon dioxide. The precipitate (0.3 g.) melted at 161–162° after crystallization from 5 ml. of absolute ethanol.

α-2-Bromomercuricineole. When an ethanolic solution of α-chloromercuricineole was treated with aqueous sodium bromide the precipitate melted at 152°. This α-bromomercuricineole was crystallized repeatedly from the hot 95% ethanol (11 ml. per g.), m.p. 152.6°.

Anal. Calcd. for $C_{10}H_{17}OHgBr$: C, 27.7; H, 3.84. Found: C, 27.6; H, 3.86.

The X-ray diffraction pattern was [10] 12.55; [9] 5.94; [6] 4.49, 3.27; [5] 3.88; [4] 4.94, 2.58; [3] 7.34, 6.73; [2] 4.17, 3.57, 3.38, 3.10, 3.02, 2.97; [1] 2.84; [0.5] 5.30, 4.76, 2.66, 2.50, 2.41, 2.34, 2.28, 2.22, 2.11, 2.00, 1.97, 1.92, 1.87, 1.82, 1.76, 1.66, 1.63, 1.59, 1.56.

Polymorphic α-2-iodomercuri-trans-terpins. The solution from which the 2-iodomercuricineole was filtered according to the foregoing procedure *B* was saturated with gaseous carbon dioxide at 0°. This precipitated a gummy solid (31 g., 62%) which was filtered off at the same temperature. It was redissolved in 150 ml. of warm 10% aqueous sodium hydroxide and was reprecipitated by gaseous carbon dioxide at 0°. This compound, evidently Sand and Singer's labile isomer, weighed 27 g. and melted indefinitely at 45–48°. Its X-ray diffraction pattern was determined: [10] 7.52; [7] 5.50; [4] 6.75; [2] 4.53, 4.15; [1] 3.78, 3.46, 3.37. After four days in dry vacuum it melted at 89–94°. Two crystallizations of either the product melting at 45–48° or that melting at 89–94° from hot benzene (15 ml. per g.) raised the melting point to 142–144°. This stable isomer was found to be identical with 3.0 g. (6%) of the precipitate collected 12 hr. after the labile isomer was precipitated by carbon dioxide. Identity was established by mixed melting point and by X-ray diffraction pattern: [10] 9.93; [8] 7.82; [5] 5.68; [3] 6.91, 5.90 (?), 4.07; [2] 11.18, 4.25, 3.69; [1] 12.99, 4.41, 3.85, 3.62; [0.5] 6.51, 5.27, 4.98, 4.72, 3.49, 3.40, 2.98, 2.79, 2.69, 2.59, 2.45. When this polymorph melting at 142–144° was dissolved in 40% aqueous potassium hydroxide (2 g. per 40 ml.) and the ice-cold filtered solution was treated with carbon dioxide a turbidity appeared. If a seed of the identical polymorph was added, only this high-melting form was precipitated. On the other hand a seed of the material melting at 45–48° caused the exclusive crystallization of the low-melting form, identified by its diffraction pattern.

2-Chloromercuri-trans-terpin. To 5.0 g. (0.01 mole) of 2-iodomercuri-*trans*-terpin, m.p. 140–142°, suspended in 25 ml. of water and 25 ml. of ethanol was added 2.0 g. (0.012 mole) of silver acetate. The mixture was stirred vigorously overnight. The yellowish-grey precipitate was removed and the filtrate was treated with 20 ml. of 10% sodium hydroxide solution which precipitated a little black solid. This was filtered off and the filtrate was treated with 25 ml. of saturated sodium chloride solution, and then was carbonated at 0°. A small quantity of grey-white precipitate was removed and the filtrate was extracted several times with chloroform. The combined extracts, after drying, were evaporated to dryness and the resulting gum was treated with a little ether which caused crystallization. This crude 2-chloromercuri-*trans*-terpin, m.p. 135–150°, weighed 2.5 g. (62%). Recrystallization from 3:1 benzene:acetone (15 ml./g.) raised the m.p. to 162–164°.

Anal. Calcd. for $C_{10}H_{19}O_2HgCl$: C, 29.5; H, 4.66. Found: C, 29.9; H, 4.85.

The X-ray diffraction pattern was: [10] 11.04, 6.80; [8] 4.57; [7] 5.90, 3.07; [6] 3.23; [5] 8.58, 2.79; [4] 3.17; [2] 5.53, 3.75, 3.60, 3.48, 2.94, 2.71; [1] 7.99, 4.23, 3.98, 2.42, 2.39, 2.29, 1.89, 1.71; [0.5] 5.06, 2.58, 2.53, 2.21, 2.16. In another experiment, which we cannot yet repeat and which involved a slow deposition out of ethanolic solution, we obtained a product of m.p. 134.5–135.5° of correct elemental composition which gave a different diffraction pattern, in part [10] 9.11; [7] 4.24; [6] 5.14, 3.81; [4] 7.39; [3] 6.21, after crystallization from benzene.

A melting point-composition diagram for α-2-iodomercuri-*trans*-terpin, m.p. 143°, and α-2-chloromercuri-*trans*-terpin, m.p. 164°, showed a continuous solid-solution curve, m.p. 145° at 25%, 148° at 50%, 152° at 75% and 157° at 90% of the chloromercurial.

Effect of pH on the yields of 2-iodomercuri-trans-terpin and 2-iodomercuricineole from mercuric nitrate and Δ^1-terpineol (by Paul Chu). The preparation was modified as follows in order to study the effect of *p*H on the yields of the various products. A mixture of 7.7 g. (0.05 mole) of Δ^1-terpineol in 70 ml. of warm water was placed in a three necked flask provided with a stirrer. Aqueous mercuric nitrate (prepared by dissolving 10.8 g. (0.05 mole) of mercuric oxide in 40 ml. in 20% nitric acid) and 10% potassium hydroxide solutions were added from two separatory funnels over about 15 min. The reaction was worked up as described above.

When the reagents were added so that a small amount of mercuric oxide was always present (about *p*H 3) the yields of 2-iodomercuri-*trans*-terpin and 2-iodomercuricineole were 56% and 25% respectively.

When an equivalent of sodium acetate was included in the mercurating system as a buffer so that the *p*H was about 4–5, the corresponding yields were 40% and 37.5%.

When the *p*H was maintained at about 6, much mercuric oxide was present and the yields were 24% and 39% respectively. Above this *p*H so much mercuric oxide formed that the yields of both products were greatly decreased.

β-2-Chloromercuricineole. To a solution of 19.4 g. (0.05 mole) of α-chloromercuricineole in 200 ml. (0.25 mole) of 5% aqueous sodium hydroxide was added 0.25 ml. (0.004 mole) of 85% hydrazine hydrate and the whole was boiled under reflux for 130 min. The reaction mixture was cooled and extracted with ether; this extract was eventually discarded. The aqueous layer was filtered to remove metallic mercury and was acidified to *p*H 4 with 12% hydrochloric acid. After 10 min. this suspension was made alkaline with 30 ml. of 10% aqueous sodium hydroxide and boiled until the odor of Δ^1-terpineol was no longer apparent. The black suspension was filtered off and the cooled filtrate was acidified to *p*H 5 with 12% hydrochloric acid. Ether was added and then evaporated to coagulate the precipitate. The crude β-chloromercurial which was filtered off weighed 9.95 g., m.p. 86–7°. This was purified by solution in alkali, etherous extraction of the alkaline solution, and then re-acidification to *p*H 5. In this way 6.78 g. (35% of theoretical) of β-2-chloromercuricineole was obtained, m.p. 101.7–102.3°. This was crystallized from 95% ethanol (15 ml. per g.) with addition of Nuchar, m.p. 104.5°. The X-ray diffraction pattern was: [10] 12.80; [9] 5.55; [6] 6.37; [4] 4.74; [3] 3.81, 3.64, 3.50, 3.06; [2] 2.59; [1] 4.25, 3.17, 2.97, 2.93, 2.82, 2.77, 2.63, 2.53, 2.50, 2.33, 2.21, 1.93, 1.89; [0.5] 5.21, 2.27, 2.15, 1.98.

TABLE I

ELECTRIC POLARIZATION DATA IN DIOXANE AT 20°

Substance	α	β	P_T	P_{E+A}	R_D	D_4^{20}	μ, D
α-Chloromercuricineole	4.06	0.458	314.8	68.5		2.099	3.42
β-Chloromercuricineole	7.85	0.442	556.8	66.9		2.197	4.82
α-Iodomercuri-*trans*-terpin	4.80	0.565	447.0		73.2		4.21
β-Iodomercuri-*trans*-terpin	5.60	0.545	516.5		73.2		4.59

Anal. Calcd. for $C_{10}H_{17}OHgCl$: C, 30.9; H, 4.37. Found: C, 31.3; H, 4.56.

When the amount of hydrazine hydrate was doubled, the crude product (5.8 g., 30%) melted at 100–101°. Further increase in amount of hydrazine hydrate caused the formation of cineole. Thus a 20-fold molar excess of the hydrate gave steam-distillable cineole in 10% yield. This product (b.p. 63°/15 mm., n_D^{25} 1.4579) was identified by its crystalline derivative with *o*-cresol.[7]

Diastereomeric chloromercuricineoles with hydrochloric acid. A mixture of 0.1 g. each of α- and β-chloromercuricineole in 2.5 ml. of methanol was treated with 0.05 ml. of concentrated hydrochloric acid for 1 min., then diluted to 4.5 ml. with water, and neutralized to *p*H 4 with alkali. The precipitate, weighing 0.07 g., was filtered and washed with petroleum ether. It was pure β-chloromercuricineole, m.p. 103–104°. The α-chloromercuricineole was converted chiefly to Δ^1-terpineol.

When 3.89 g. (0.01 mole) of the α-diastereomer was treated with 0.1 ml. of concentrated hydrochloric acid and 10 ml. of methanol for 20 min. a 90% yield of dipentene dihydrochloride, m.p. 48° (crystallized from petroleum ether, m.p. 52.8°), could be filtered off. This was identified by mixture melting point with the identical product of Δ^1-terpineol and concentrated hydrochloric acid. Under the same conditions the β-chloromercuricineole was recovered unchanged.

Oxidation of α-chloromercuricineole. A solution of 3.89 g. (0.01 mole) of α-chloromercuricineole in 32 ml. of 3% aqueous sodium hydroxide was treated with 10 g. (0.063 mole) of potassium permanganate in 150 ml. of water over 75 min. The excess was destroyed with methanol and the manganese dioxide was filtered off. The filtrate was saturated with carbon dioxide to demonstrate that no mercurial remained and then was concentrated to a volume of 15 ml. and acidified to *p*H 2.7. The precipitate (cineolic acid) weighed 1.72 g. (80%), m.p. 202–203°. Crystallization from hot water (30 ml. per g.) raised the melting point to 207°.

Anal. Calcd. for $C_{10}H_6O_5$: C, 55.3; H, 7.47. Found: C, 55.5; H, 7.54.

β-Bromomercuricineole. An ethanolic solution of the β-chloromercuricineole was shaken for 12 hr. with one equivalent of silver acetate and the filtrate drowned with sodium bromide. The precipitate was crystallized from hot 95% ethanol (5 ml. per g.) with addition of Nuchar, m.p. 113–114°.

Anal. Calcd. for $C_{10}H_{17}OHgBr$: C, 27.7; H, 3.84. Found: C, 27.6; H, 3.97.

The X-ray diffraction pattern was: [10] 13.18; [9] 5.59, 3.85, 3.70; [8] 6.49, 3.55, 3.20; [6] 2.67; [4] 4.78; [3] 4.34; [2] 1.86; [1] 5.21, 3.32, 3.12, 2.79, 2.59, 2.52, 2.36, 2.32, 2.24, 2.19, 2.09, 1.92, 1.77; [0.5] 3.44, 2.99, 2.15, 2.03, 1.98, 1.95, 1.89, 1.81, 1.73, 1.66, 1.63, 1.59, 1.55, 1.49, 1.43, 1.38, 1.30, 1.28, 1.24.

β-Iodomercuricineole. The ethanolic solution of acetoxymercuricineole (described above) was treated with sodium iodide. The product was crystallized from hot 95% ethanol (5 ml. per g.), m.p. 116–117°.

Anal. Calcd. for $C_{10}H_{17}OHgI$: C, 25.0; H, 3.56. Found: C, 25.8; H, 3.28.

The X-ray diffraction pattern was: [10] 13.38; [9] 3.86; [5] 6.65, 5.67, 3.75, 3.61; [4] 3.02, 2.62; [2] 4.74, 2.53, 1.96; [1] 5.20, 4.45, 4.30, 3.16, 2.73, 2.33, 2.24, 2.17, 2.13, 2.01, 1.92, 1.81, 1.70, 1.63; [0.5] 3.41, 3.27, 2.90, 2.79, 2.37, 2.08, 1.85, 1.76, 1.65, 1.58, 1.52, 1.49, 1.45.

β-Iodomercuri-trans-terpin. A solution of 4.98 g. (0.01 mole) of α-iodomercuri-*trans*-terpin in 32 ml. (0.02 mole) of 2.5% aqueous sodium hydroxide was warmed to 60° and then 0.05 ml. (0.001 mole) of 85% hydrazine hydrate was added. After 12 hr. at room temperature the system was diluted to 200 ml. volume and reheated to dissolve the white precipitate and was then filtered to remove mercury. Addition of gaseous carbon dioxide to the filtrate precipitated 3.35 g. of mercurial mixture melting below 80°. The aqueous phase was extracted with chloroform; this residue from evaporation of the extract was combined with the solid product and dissolved in 25 ml. of methanol. This solution was cooled to 0°, then treated with 1 ml. of concentrated aqueous hydriodic acid for exactly 1 min., and then was diluted with 60 ml. of 2% aqueous sodium hydroxide. This suspension was boiled until the odor of terpineol was no longer apparent. After replacement of the water which had distilled over, the remainder was partially cooled and filtered. The cold filtrate was acidified with hydriodic acid and extracted with five 10-ml. portions of chloroform. The extract was evaporated and the residue crystallized from 30 ml. of hot benzene; 0.6 g., m.p. 158–159°. This 12% yield was thrice crystallized from benzene (42 ml. per g., 85% recovery), m.p. 161.8–162.2°. When the compound was heated for 1 hr. in pyridine at 60–70°, dilution with ether precipitated it unchanged.

Anal. Calcd. for $C_{10}H_{19}O_2HgI$: C, 24.1; H, 3.84. Found: C, 24.4; H, 3.95.

Reduction of 0.3 g. (0.0062 mole) of this β-mercurial with 2 g. (0.0017 atom) of 2% sodium amalgam in 2.5 ml. of water during 9 hr. yielded by exhaustive ether extraction 0.12 g. (50%) of *trans*-terpin, m.p. 155–156°, depressed by admixture with the β-mercurial to 135°.

Dielectric constant determinations. An apparatus described previously[9] was used for these studies. The solvent, dioxane, had a dielectric constant of 2.2210 and a specific volume of 0.9681 at 20°. Extrapolation of the $d\epsilon/d\omega(\alpha)$ and $dV/d\omega(\beta)$ plot to $\omega = 0$ gave intercepts in close agreement with ϵ and V for the pure solvent. Combined electronic and atomic polarizations as well as densities were determined as described previously,[10] while molecular refraction (R_D) was calculated additively. Significant data are recorded in Table I.

β-2-Acetoxymercuri-trans-terpin. A mixture of 2.49 g. (0.005 mole) of β-iodomercuri-*trans*-terpin and 11.5 g. (0.05 mole) of silver oxide in 70 ml. of acetone plus 5 ml. of water was shaken for 12 hr. and then filtered. The filtrate was vacuum-evaporated leaving 1.87 g. of non-crystalline residue which was dissolved in 5.2 ml. (0.05 mole) of acetic anhydride and filtered at once. Within 10 min. crystals began to appear. After 2 hr. filtration yielded 1.53 g., m.p. 129.5–130° (65%) which was crystallized from 7 ml. of toluene, 1.19 g., m.p. 130°. Treatment with aqueous sodium chloride converted this compound to 2-chloromercuri-*trans*-terpin, m.p. 120.5–121°, authenticated by mixture melting point.

Anal. Calcd. for $C_{12}H_{22}O_4Hg$: C, 33.4; H, 5.15. Found: C, 33.8; H, 5.26.

β-2-Chloromercuri-trans-terpin. A solution of 0.6 g. of the acetoxymercuri analog in 6 ml. of chloroform was shaken with saturated aqueous sodium chloride. The crystalline substance (0.48 g.) which precipitated from the nonaqueous layer melted at 120–120.6° and was unchanged in melting point by crystallization (2 ml. per g.) from hot chloroform.

Anal. Calcd. for $C_{10}H_{19}O_2HgCl$: C, 29.5; H, 4.70. Found: C, 29.3; H, 4.51.

Bis-β-2-mercuri-trans-terpin sulfide. A solution of 2.49 g. (0.005 mole) of β-2-iodomercuri-*trans*-terpin in 65 ml. of acetone was treated with 0.4 ml. (0.0066 mole) of acetic acid and then 1.20 g. (0.005 mole) of sodium sulfide nonahydrate in 6 ml. of water was added. After a day the solvent was evaporated leaving a filterable residue, 1.72 g. (88%), m.p. 190°. Solution in dimethylsulfoxide (10 ml. per g.) followed by addition of one-half volume of water raised this melting point to 194–194.5°. After 3 hr. of reflux in methanol 55% was recovered unchanged. Treatment with lead acetate trihydrate in acetic acid precipitated lead acetate at once yielding a complex product, m.p. 134–138°.

Anal. Calcd. for $C_{20}H_{38}Hg_2O_4S$: C, 30.9; H, 4.97; S, 4.13. Found: C, 30.6; H, 4.95; S, 4.30.

By contrast to the preparation of this sulfide the same reaction conditions applied to α-iodomercuri-*trans*-terpin yielded only terpineol.

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TORONTO, CANADA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE STATE UNIVERSITY OF IOWA]

Model Compounds for Comparison with Lignin.* I. Preparation and Properties of 8-Methoxy-6-methylflavanone and 2′-Hydroxy-3′-methoxy-5′-methylchalcone

MERVIN F. BROWNE[1] AND R. L. SHRINER

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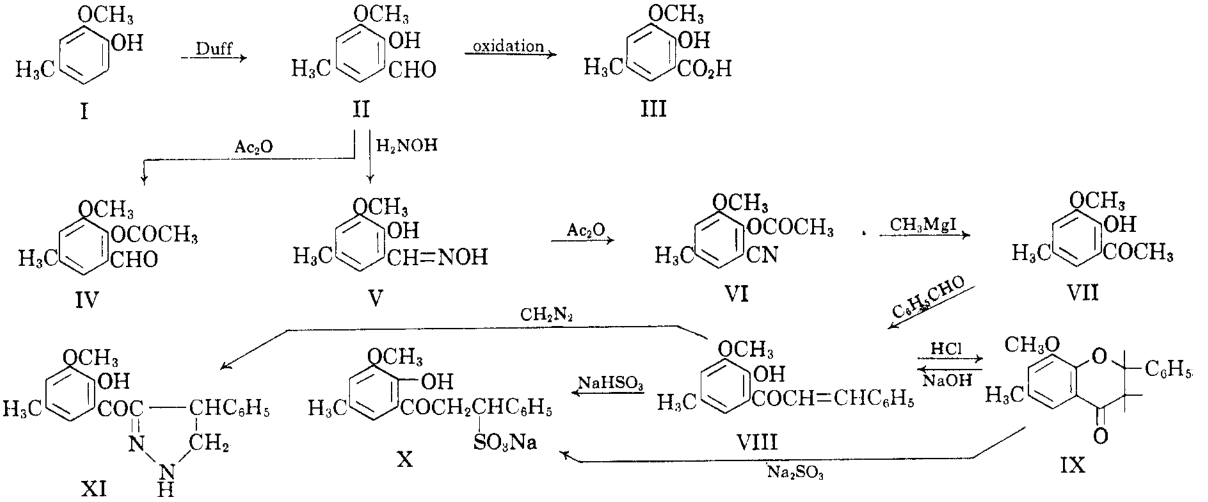
The syntheses of 8-methoxy-6-methylflavanone and 2′-hydroxy-3′-methoxy-5′-methylchalcone are described. These compounds differed from those reported for soft wood lignin with respect to ultraviolet and infrared spectra and also in their chemical properties.

Brauns[2] and Harris[3] have reviewed the various structures proposed for spruce lignin. One of the polymeric structures incorporated a substituted chalcone unit in equilibrium with the flavanone unit.[4,5] For purposes of comparison, two model compounds, 2′-hydroxy-3′-methoxy-5′-methylchalcone (VIII) and 8-methoxy-6-methylflavanone (IX) have been prepared and their properties compared with some of the reactions reported for lignin. Chart I summarizes the reactions and inter-



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[*] A contribution in honor of Lyndon F. Small and a tribute to his services as former Editor of this Journal, as Chairman and member of the Executive Committee of the Division of Organic Chemistry and for his outstanding investigations in organic chemistry.

(1) From the Ph.D. Thesis submitted to the Graduate College of the State University of Iowa.

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