

Part I.—A new Method for the Production of Terpin Hydrate¹

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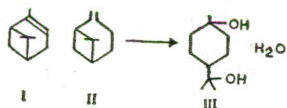
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A systematic study of the production conditions for terpin hydrate has been carried out. The application of either benzene- or toluene sulphonic acid has advantageously eliminated the use of sulphuric acid in the existing processes. In contrast to sulphuric acid, the sulphonic acids do not require the presence of additional emulsifiers and the maintenance of costly conditions of low temperature and inert atmosphere. The yield of the hydrate with either acid is also always higher than that obtained with sulphuric acid.

Introduction

Terpin hydrate is an important intermediary product in the manufacture of commercial terpineol. It is also used in the pharmaceutical preparations to inhibit cough and expectoration in chronic bronchitis, and is administered in an elixir.²

Terpin hydrate, terpineol and pine oil are obtained as a result of hydration of α - and β -pinenes (I and II), generally occurring in different quantities, in turpentine oils. *cis*-Terpin hydrate (III) can be obtained quite readily in the crystalline form when turpentine oil is allowed to react with sulphuric acid under controlled conditions. In one of the methods,³ the reactants are vigorously shaken for periods extending well over ninety hours. The resulting crystalline terpin hydrate is separated from the reaction mixture by centrifuging and washing with dilute ammonia and water in order to remove the adhering acid and the unreacted oil. In the modified methods,^{4,5} sulphuric acid is used again but in the presence of various emulsifying agents such as gelatine and gums, sulphonates and sulphonic acids. There is, however, no obvious improvement in the yield of the product.



Since concentrated sulphuric acid is basically a dehydrating agent, its use in this reaction always requires the adoption of special measures^{3,6} which include slow dropwise addition of the acid, maintenance of low temperature and continuous vigorous stirring of the reactants. Another condition is to keep the reactants under an inert atmosphere. A little rise in temperature, for instance, results in the polymerisation of turpen-

tine oil and in the formation of other undesirable side-products, thereby affecting the yield of terpin hydrate.

The maintenance of these conditions, particularly of low temperature and inert atmosphere in sulphuric acid hydration, is obviously a costly as well as tedious step. Its elimination, therefore, would considerably simplify the procedure for the production of terpin hydrate. A successful attempt has been made to prepare terpin hydrate from *Pinus longifolia* turpentine oil at room temperatures (16-35°), by replacing sulphuric acid with benzene- or toluene sulphonic acid which acts simultaneously as a mild hydrating as well as emulsifying agent.

In this paper, the production conditions for terpin hydrate with the sulphonic acids have been described.

Materials and Methods

Materials.—Turpentine oil: Turpentine oil, Grade I, obtained from the Jallo Rosin and Turpentine Factory, was employed in these studies.

Acids and Sulphates: The various acids and sulphates were of commercial grade.

Reaction Vessel.—The conversion of the turpentine oil pinenes into terpin hydrate was carried out in a 3-litre stainless steel drum which had a removable lid. The drum when mounted on its horizontal axis could be revolved with an electric motor at 40 r.p.m.

Procedure

500 g. of the turpentine oil and known amounts of the hydrating agents particulars of which are recorded in the Results were placed in the reaction vessel. The lid of the vessel was closed tightly and the reactants were thoroughly shaken for

different periods of time. Subsequently, the vessel was allowed to rest till the emulsion, arising from the vigorous shaking, broke up and terpin hydrate separated out in the crystalline form. The products were drawn off from the vessel and filtered through a Buchner funnel under suction of a water pump. The crystals left on the funnel were washed with water several times and dried in an oven at 60-70°. The percentage yield of the hydrate as obtained with different reagents is recorded under the Results (Tables 1 to 3).

TABLE 1.—THE YIELD OF TERPIN HYDRATE WITH VARIOUS SULPHONIC ACIDS (32% AQUEOUS SOLUTIONS).

Acid	Percentage yield of terpin hydrate
Benzene sulphonic acid	62.8
Toluene sulphonic acid	61.5
p-Phenol sulphonic acid	49.6
Sulphosalicylic acid	34.2
Dodecyl benzene sulphonic acid	Negligible
Sulphamic acid	12.6
Naphthol sulphonic acid	Negligible
Amberlite resin IR-120 (H ⁺)	19.0

Discussion and Conclusions

Since no composition data for the Pakistani *Pinus longifolia* turpentine oil were available, all the grades of the oil obtained from the Jallo Factory, were, therefore, analysed by gas-liquid phase chromatography (GLC). The analysis was carried out by a conventional GLC isothermal unit using T/C detectors and a non-polar column. A 5 ft. × ¼ in. glass column filled with celite (80-120 mesh) containing 5% by weight of silicon elastomer 301, operated at 160° and 20 ml./min. nitrogen was used for the separation of the oil constituents.

Grade I had the highest pinene contents (Table 4) and was, therefore, used as the starting material throughout these investigations.

TABLE 2.—THE YIELD OF TERPIN HYDRATE WITH DIFFERENT CONCENTRATIONS OF BENZENE- AND TOLUENE SULPHONIC ACIDS.

Concentration	Percentage yield of terpin hydrate with	
	Benzene sulphonic acid	Toluene sulphonic acid
10%	Negligible	nil
20%	28.9	25.6
30%	62.6	61.2
40%	62.0	62.7
50%	61.5	61.8

TABLE 3.—THE YIELD OF TERPIN HYDRATE WHEN 32% BENZENE SULPHONIC ACID SOLUTION IS SHAKEN FOR DIFFERENT PERIODS WITH TURPENTINE OIL IN 1.5:1 RATIO.

Shaking periods in hour	Percent yeild of terpin hydrate						
	40	50	60	70	80	90	100
	45.8	48.5	52.6	58.3	61.7	62.8	62.9

While employing sulphuric acid alone it was observed that the maximum yield of terpin hydrate could only be obtained when the concentration of the acid was 53% and the temperature of the reaction mixture-12°.

The use of either metallic sulphates viz. Cr(3), Co(2), Cu(2), Fe(2), Mn(2), and Ni(2), as catalysts alongwith sulphuric acid or a cation exchange resin IR-120 (H⁺) alone did not improve the production conditions.

It was found (Table 1) that benzene - and toluene sulphonic acids give 62.8 percent and 61.5 percent yields of terpin hydrate respectively. For the rest of the sulphonic acids, the yields were

TABLE 4.—COMPOSITION OF THE DIFFERENT GRADES OF *Pinus longifolia* TURPENTINE OIL BY GLC.

Grade	α -pinene %	β -pinene %	Δ^3 -carene %	longi- folene %
I	32.6	19.8	47.5	nil
II	23.6	9.5	61.7	6.07
III	nil	21.3	67.8	10.9

low; but, comparatively, p-phenol sulphonic acid gives as good a yield as that obtained with sulphuric acid alone. The effectiveness of benzene sulphonic acid over sulphuric acid for the production of terpin hydrate was further demonstrated when sulphuric acid, equivalent in amount to that present in 30% aqueous solution of benzenes sulphonic acid, was shaken at room temperature for 90 hours with turpentine oil containing alcohol as an emulsifier, the maximum yield of the hydrate was only 33 percent.

It was noticed that the yield of terpin hydrate was maximum when (1) the concentration of benzene- and toluene sulphonic acids was 30 percent and 40 percent respectively (Table 2), (2) the ratio of 32 percent solution of benzene sulphonic acid to turpentine oil was 1.5:1 and (3) the reaction mixture was shaken for ninety hours at room temperatures (Table 3).

References

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