

PHYTOCHEMICAL NOTES.

80. *A Crystalline Resin Acid From Pinus Sabiniana.*

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The oleoresin of Digger's pine has heretofore attracted the attention of the phytochemist because of its heptane content. If the exploiters for naval supplies in California at the time of the civil war were disappointed in finding that the so-called gum yielded no turpentine, exploiters for rosin may have been equally disappointed in finding that the oleoresin from this species, when distilled, yielded a sticky and unsightly resin or rosin. If, however, either resin or oleoresin be subjected to distillation under diminished pressure, a transparent, hard and amber-colored resin is obtained. So far as appearance is concerned this resin can readily compete with the first grades of rosin on the market.

As already indicated, the oleoresin can be used as well as the resin obtained by steam distillation of the oleoresin. Inasmuch as the resin contained chips, etc., admixtures introduced during the collecting of the oleoresin, the resin was dissolved in alcohol and the solution filtered. The resin obtained after the evaporation of the solvent was clear and hard. The oleoresin which was used in another experiment was not purified but distilled as it came from the trees. The oleoresin used in these experiments was obtained through the co-operation of Mr. Garvey Cline, Director of the Forest Products Laboratory, at Madison, Wisc.

One hundred grams of material were used in each experiment. The distillation was carried on in an ordinary round-bottom distilling flask. The distillate began to come over at a temperature of about 220°. In the case of the resin the maximum temperature was reached at 240°, while the oleoresin could be distilled to 260°, without any decomposition. The pressure in both cases was kept fairly constant at 18-20 mm.

The distillate upon cooling became very hard in both cases. That obtained from the resin was taken up with acetone and allowed to evaporate slowly. In a few days crystals were observed in the mother liquor. The supernatant liquid was removed with the aid of alcohol and the crystals were collected on a force filter. Recrystallized from acetone, the resin acid from both sources was found to melt between 152°-155° C. Lack of time and the small amount of material thus far prepared have prevented an investigation of this crystalline resin acid for the present.

A word of comment concerning what some may regard as a rather queer behavior may not be out of place. Distillation of a resin or high molecular resin acid, even when conducted under diminished pressure, may be supposed to yield decomposition products rather than to change a semi-natural product that refuses to crystallize into one that will crystallize. Neither will the suggestion that fractional distillation under diminished pressure has improved the situation explain very much if one recalls the failure of attempted fractional crystallization. The explanation will have to be sought elsewhere.

The resin acids possibly find their closest analogues in organic chemistry in the so-called terpenes and related compounds. Now, it is well known to the

terpene chemist that in not a few instances the capacity for crystallization is much greater on the part of the optically inactive member of a group of optical isomers than on the part of the two optically active representatives of the same group.

In like manner the melting point of such inactive substance has frequently been found to be higher than the active components. In one instance, the writer, while working in Wallach's laboratory in Goettingen in 1889-1890, made use of these observations in the identification of an optically active substance of which but an exceedingly small amount was available. A few years later, it was observed in this laboratory that optically active resin acid from black pitch can be distilled under diminished pressure without other important change than loss of its optical activity.* Hence the distillation of the Digger's pine resin suggested itself with the results recorded above. The explanation proposed with regard to the capacity of crystallization may also throw light on the variation of the melting point observed in connection with some of the resin acids, e. g. abietic acid. A careful study of the optical activity and melting point of resin acids would therefore, seem very desirable.

The technique of resin research is not without its difficulties. Probably most of the work recorded in literature has been performed with amorphous material. Chemical literature may be overburdened but scarcely enriched by such contributions. To have been able, therefore, to cause the Digger's pine oleoresin to give up one of its constituents in crystalline form was a welcome result to one who for years had been watching solutions in various solvents with the hope that one of them might show a slight inclination to crystallize. In this particular instance the work undertaken during the past year was doubly fortunate in as much as it revealed a second method whereby a crystalline resin acid could be obtained from the Digger's pine. Again the success was due to a slight modification in the technique.

The precipitation of the resin acid as lead salt and its regeneration in the customary manner having failed to yield any crystalline products on a previous occasion, fractional precipitation was resorted to. But, as will be shown, even this precaution did not yield the desired results when the acid was regenerated according to the conventional methods.

A portion of resin from Digger's pine was dissolved in alcohol, filtered, and placed in a large wide mouthed bottle. Six fractional precipitates of the lead salt were made by adding alcoholic lead acetate. After the sixth addition of lead acetate and the removal of the corresponding precipitate no more lead salt was thrown down by the addition of lead acetate. The precipitates were thoroughly dried and the lead content of each determined as lead oxide.

	Percent as PbO	
	I	II
Precipitate No. I	4.90 p.c.	4.82 p.c.
Precipitate No. II	10.81 p.c.	10.74 p.c.
Precipitate No. III	14.55 p.c.	14.64 p.c.
Precipitate No. IV	18.45 p.c.	18.40 p.c.
Precipitate No. V	19.32 p.c.	19.28 p.c.
Precipitate No. VI	20.56 p.c.	20.51 p.c.

*Proc. Wisc. Ph. A., 13 (1892), p. 48.

The final filtrate from the lead acetate precipitates was treated as follows: additional fractional precipitates were obtained by adding aqueous lead subacetate until no further precipitate was formed. The mother liquor was set aside in a cool place and left for several weeks. Gradually a white crystalline solid was formed which deposited upon the sides of the bottle. Upon determination of the lead as oxide in the compound so formed it was found to be 53.3 p. c. PbO . This is approximately the same as the theoretical percentage of lead oxide corresponding to the lead abietate, $(\text{C}_{20}\text{H}_{27}\text{O}_2)_2 \text{PbO}$.

The lead salt obtained from the sixth precipitation with alcoholic lead acetate was used to secure a resin acid.

1. 100 grams of the lead precipitate were treated with twice the amount of sulphuric acid as ethyl sulphate necessary to precipitate the lead in the sample. The mixture was stirred and allowed to stand over night. The solution was filtered from the precipitate of lead sulphate. The filtrate upon standing did not yield any crystals, but dried to an amorphous mass.

2. An attempt to regenerate the acid by precipitating the lead as sulphide from the alcoholic mixture likewise gave only amorphous products.

3. Another 100 grams of lead precipitate were treated with a hydrochloric acid solution of alcohol. An equivalent quantity of this solution was added to the lead salt. The precipitate was filtered off and the filtrate was set aside and allowed to evaporate slowly. After about two weeks crystals were observed in the mother liquor. The syrupy liquid surrounding the crystals was removed by washing with a mixture of acetic acid and acetone. The resin acid was then purified by recrystallization from pure acetone.

The melting point was found to be between $145\text{--}150^\circ\text{C}$, after the third crystallization.

Several solvents were used for the purification of the resin acids, viz.: acetone, amyl alcohol, ethyl alcohol, methyl alcohol, ether, chloroform, ethyl acetate and acetic acid. All but the acetone proved to be unsatisfactory for the separation of the mother liquor from the resin acid.

In this case also the amount of crystalline material obtained thus far was small. Neither did the time permit of a more careful investigation at present. Hence even the question as to the identity of the two crystalline acids obtained by different methods from the same material remains unanswered. The same source, also the proximity of the melting points would seem to indicate identity. If what has been said in commenting on the fractional distillation method be borne in mind, the somewhat higher melting point of the acid obtained by the first method will be readily understood.

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