

IV. *On Larixinic Acid, a crystallizable volatile principle found in the Bark of the Larch Tree (Pinus Larix, Linn.).* By Dr. JOHN STENHOUSE, F.R.S.

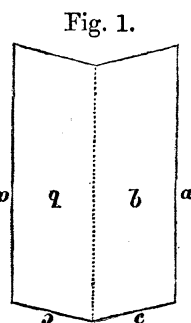
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THE most convenient way of preparing this somewhat singular substance consists in cutting the bark of the larch into small pieces, and then digesting it in water for twenty-four hours at a temperature of about 80° Cent. The solution, which has a deep reddish-brown colour, is then poured off on to a second portion of larch bark and digested as before. The concentrated infusion is then cautiously heated in an open porcelain dish, at the temperature of about 80° Cent., till it is converted into a syrup. A portion of this syrup is then distilled, either in glass or porcelain retorts, or, what is better than either, in a silver alembic. Iron retorts cannot be employed for this purpose, as the acetic acid which is always produced during distillation, by forming acetate of iron, instantly destroys the larixinic acid, by changing it into a deep-purple-coloured liquid. When a silver alembic cannot be procured, a very convenient way of distilling the extract of the larch is to pour it into a large Florence flask, the neck of which is passed obliquely through a cork or bung, which is inserted into a glass condenser. When the flask is cautiously heated on a sand-bath, the larixinic acid comes over with the first portions of the liquid, but becomes more abundant as the distillation proceeds, and usually forms large flat crystals which condense on the sides and neck of the receiver. The liquid which is distilled over, and which contains the greater portion of the larixinic acid, should be poured into small flat basins, and cautiously concentrated at about 60° Cent. When the greater portion of the water has been dissipated, it is advisable, especially in warm weather, to complete the operation by spontaneous evaporation; for unless the concentration of the aqueous solution of larixinic acid is conducted cautiously, the larixinic acid volatilizes along with the vapour of water, and is thereby lost. The highly concentrated solution of larixinic acid obtained in the way just described, on standing, deposits brownish-yellow crystals, which are impure larixinic acid. This is to be pressed between folds of blotting-paper, and again to be crystallized out of a small quantity of water. The larixinic acid may be rendered perfectly pure by subliming it once or twice. This is easily effected by placing the larixinic acid between two watch-glasses, or in any other suitable apparatus, and heating it cautiously on a sand-bath, or even on a water-bath, as the larixinic acid sublimes at the very low temperature of 93° Cent. The larixinic acid is a proximate principle, which exists ready formed in the larch. This is easily proved by distilling even a dilute infusion of the bark, when the liquid which passes over will be found to strike a deep purple colour with a persalt of

iron, which is very persistent. The bark of old larch trees contains very little larixinic acid; but the bark of the small branches, and that of the stems of the larch when not more than from twenty to thirty years of age, contains very considerable quantities of this substance, the concentrated syrup from the portions of bark yielding more larixinic acid than an equal weight of catechu does of oxyphenic acid. Larixinic acid, after it has been purified by sublimation, forms beautifully white crystals, often more than an inch in length, of a brilliant silvery lustre, very much resembling benzoic acid in appearance. They sublime at  $93^{\circ}$  Cent., and melt at  $153^{\circ}$  Cent.; but its aqueous solutions volatilize at ordinary temperatures. I am indebted to the kindness of Professor W. H. MILLER, of Cambridge, for the subjoined measurements of the crystals of larixinic acid.

“The crystals obtained by sublimation become rough so rapidly when exposed to the air, that very little confidence can be placed in the following results:—

“The crystals belong to the oblique system; they usually occur in twins, like the annexed figure. They are extremely thin in a direction perpendicular to  $b$ . Denoting by  $l, m, n$  faces in the zone  $ab$ , and by  $r$  a face in the zone  $bc$ , it appears that  $\tan bl, \tan bm, \tan bn$  are nearly as the numbers 2, 3, 6, and that  $ab=90^{\circ} 0', bc=90^{\circ} 0', ac=76^{\circ} 0', bl=49^{\circ} 29', bm=60^{\circ} 20', bn=74^{\circ} 6', br=75^{\circ} 30'$ . Cleavage  $a$  distinct,  $c$  imperfect.



“The crystals of larixinic acid crystallized out of water are very imperfect; the angles must be regarded as very rough approximations. They are deduced, as well as I could deduce them, from a mean of a considerable number of observations by no means agreeing well with each other. The angle between the normals to two faces is taken as the measure of the angle between the faces.

“Oblique:—

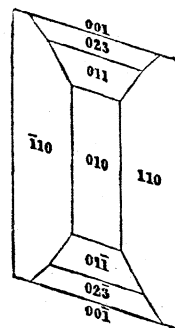
$$\begin{aligned} 100, 101 &= 26^{\circ} 22' \\ 010, 111 &= 74^{\circ} 36'; \quad 001, 101 = 44^{\circ} 20'. \end{aligned}$$

“Forms observed:—

$$010, 001, 110, 011, 023$$

Angles.	
110, 001	= 71° 58'
010, 110	= 69 35
010, 011	= 59 37
010, 023	= 68 39
010, 001	= 90 0

Fig. 2.



“Cleavage  $001$  distinct, and very easily obtained.”

The smell of the aqueous solution of larixinic acid is sweetish, like that of a syrup, but the smell of the sublimed acid is very peculiar and slightly empyreumatic. As larixinic acid emits a sensible odour at ordinary temperatures, in this respect it con-

siderably resembles naphthaline and ordinary camphor. The taste of larixinic acid is slightly bitter and astringent. It reddens litmus paper very slightly, but a single drop of potash or ammonia, when added to a solution of a large quantity of larixinic acid, renders it alkaline. Larixinic acid is very soluble in boiling water, but is by no means very soluble in cold water, 87·88 parts of water at 15° C. dissolving 1 part of the acid only; but the solubility of larixinic acid in cold aqueous solutions is greatly increased by the addition of either acids or alkalies. Larixinic acid is deposited from its aqueous solutions in crystals which are very brittle, and often an inch or two in length. It likewise dissolves in cold alcohol, but to a much greater extent in hot alcohol. The crystals deposited from its alcoholic solutions are thicker and more distinctly formed than those from water. It also dissolves but sparingly in ether, and is deposited in crystals of very considerable lustre\*. The following are the results of the analysis of the larixinic acid:—

- I. 0·221 sublimed acid, dried *in vacuo*, gave 0·4633 carbonic acid and 0·1003 water.  
 II. 0·1993 sublimed acid, dried *in vacuo*, gave 0·417 carbonic acid and 0·0913 water.  
 III. 0·2272 larixinic acid, crystallized out of water, gave 0·4756 carbonic acid and 0·1030 water.

Calculated numbers.		Found.		
		I.	II.	III.
C <sub>20</sub>	= 57·14	57·13	57·06	57·09
H <sub>10</sub>	= 4·77	5·04	5·09	5·04
O <sub>10</sub>	= 38·09	37·83	37·85	37·87

From these results it is evident that the carbon, hydrogen, and oxygen in larixinic acid are in the proportion of C<sub>2</sub>H<sub>1</sub>O<sub>1</sub>, or some multiple of these numbers, C<sub>20</sub>H<sub>10</sub>O<sub>10</sub> being the numbers we have adopted as the more probable.

When a quantity of larixinic acid was dissolved in a great excess of liquid ammonia, a yellow-coloured solution was produced; when this was evaporated to dryness over sulphuric acid *in vacuo*, the larixinic acid was deposited in crystals which were nearly unaltered. It gave its characteristic reactions with salts of iron, and when boiled with milk of lime gave off no trace of ammonia. The combination which larixinic acid forms with ammonia is therefore so feeble that it is decomposed by the volatility of the ammonia. In this respect, therefore, and in its forming no hydrate, larixinic acid closely resembles both pyrogallic and oxyphenic acids.

When larixinic acid was treated with an excess of aqua potassæ it very readily dissolved, forming a yellowish solution. When dried over sulphuric acid *in vacuo*, the potash combination formed long flattish crystals having considerable lustre, but of a reddish-brown colour. These crystals, when pressed between folds of blotting-paper to free them from excess of potash and recrystallized *in vacuo*, yielded crystals which were more deeply coloured than the first. This potash combination is so very feeble that

\* The crystals of larixinic acid catch fire readily, and burn with a bright flame, leaving no residue.

it is decomposed by carbonic acid. It contained a considerable quantity of potash; but I have not been able to obtain it of a constant composition.

A solution of larixinic acid gives no precipitate, either with lime-water or with saccharate of lime. The behaviour of larixinic acid with baryta is extremely singular and characteristic. When a solution of caustic baryta is added to a concentrated aqueous solution of larixinic acid, the latter being in excess, a bulky, semitransparent, gelatinous precipitate immediately falls, and if the solutions are concentrated fills the whole vessel. This precipitate, which considerably resembles hydrated alumina, is but slightly soluble in cold water; but it dissolves very readily in boiling water, from which it is again deposited on the cooling of the liquid. This baryta compound is readily decomposed by carbonic acid. When thrown on a filter and washed, the air being carefully excluded, it was dried *in vacuo* over sulphuric acid, and was then found to contain, as the mean of two experiments, 34.92 per cent. of baryta.

A solution of larixinic acid yields no precipitate with either basic or neutral acetate of lead, neither is it precipitated by nitrate or ammonio-nitrate of silver; but when its solution in the latter salt is boiled, the silver is reduced in a pulverulent state. Larixinic acid forms no precipitate with perchloride of platinum, even on the application of heat. It does not contain any nitrogen. It does not reduce oxide of copper when tried by TROMMER'S test. It dissolves in concentrated sulphuric acid, but no conjugate combination is produced, as was ascertained by neutralizing with carbonate of baryta, larixinic acid being obtained unchanged. When larixinic acid is boiled with a mixture of hydrochloric acid and chlorate of potassa, it is decomposed, but without the formation of chloranile. When it is boiled with a solution of hypochlorite of lime, no coloration is produced. It is readily attacked by nitric acid, especially when assisted by heat; nitrous fumes are given off, and oxalic acid is the only fixed product. It is also readily attacked by bromine, especially when assisted by heat. Abundant vapours of hydrobromic acid are given off, the larixinic acid being entirely destroyed and converted into an uncrystallizable resin. The salts of copper produce an emerald-green colour in solutions of larixinic acid, but no precipitate. Chloride of manganese produces neither coloration nor precipitation. Protosulphate of iron strikes a brownish-red colour with solutions of larixinic acid, which acquire a brighter red colour on standing, resembling meconate of iron. Perchloride and persulphate of iron produce a beautiful purple dahlia-colour, which is very persistent, and stands dilution well. Its reactions with salts of iron are very characteristic of larixinic acid, which forms an excellent reagent for the detection of salts of iron, even in very minute quantity. In this way the presence of iron, in tolerably pure sulphate of copper, can readily be detected by the purple coloration produced. Larixinic acid does not affect neutral protonitrate of mercury in the cold; and on the application of heat no mercury is reduced.

Larixinic acid appears to be peculiar to the larch tree; at least I have not been able to find a trace of it in the bark of the spruce fir (*Abies excelsa*), or in that of the Scotch fir (*Pinus sylvestris*). Larixinic acid evidently belongs to that small group of substances

of which pyrogallic acid and pyrocatechine, the oxyphenic acid of GERHARDT, are the only other members yet known. Larixinic acid is much less easily oxidizable than oxyphenic acid, which again is less easily oxidated than pyrogallic acid. Larixinic acid volatilizes at a much lower temperature than either of these two substances, from which it also differs in being a ready-formed proximate principle, and not an educt.

*Addendum.*—In consequence of the extremely feeble, if not somewhat doubtful, acid properties of the so-called larixinic acid, perhaps the name *Larixine* would be more appropriate; but in that case the name of pyrogallic acid should be altered to *pyrogalline*, and that of oxyphenic acid to *pyrocatechine*, the name originally given to it by ZWENGER.—J. S.