

THE EVALUATION OF CANADA BALSAM

BY STEPHEN B. CHALLEN*

From the College of Pharmacy, University of Saskatchewan, Saskatoon, Canada

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Adulteration of commercial samples of Canada balsam with oil is reported, and methods for the detection of this are described. Fresh samples of oleoresin collected during field studies in Quebec Province have been analysed and certain natural variation in the properties of unadulterated oleoresin noted. Acid values may be correlated with the age and condition of trees from which the oleoresins were obtained.

CANADA BALSAM (Canada Turpentine, Balsam of Fir, Gomme de Sapin) is the oleoresin obtained by puncturing blisters which occur on the bark of *Abies balsamea* Mill. The chief industrial use for the oleoresin is for cementing optical lenses, and the adhesive is prepared by dissolving the resin in a suitable solvent. The resin is prepared by removing the volatile oil from the oleoresin with the aid of heat. The resin consists mainly of abietic acid (Lombard, Rotovic and Crigue, 1958; Trost, 1936) with neo-abietic acid and traces of pimaric acids (Lombard and others, 1958). The resene is neutral, inert, of undetermined constitution and is probably a mixture of substances chemically related to the resin acids. The volatile oil contains pinene and phellandrene (Petrowitz, Nerdel and Ohloff, 1962). The resin should be hard and brittle, transparent and pale in colour and have a refractive index near to that of ordinary glass (Bickford and Clark, 1933). During 1961, defective samples of the oleoresin were exported from Canada to Great Britain and the resins prepared from them were soft and sticky, and either opaque, or dark reddish brown in colour. Visual examination of the oleoresins gave little indication that they were defective, although some samples were thinner in consistency than usual. All the samples were investigated on the assumption that variation in properties was due to the presence of another foreign natural product. Fresh oleoresin collected from trees has also been compared with commercial samples.

EXPERIMENTAL

Commercial Samples

As a general test for detecting samples which were not likely to give a hard resin, the following was found useful. Approximately 5 g. of oleoresin was placed in a dish made from aluminium foil and measuring 1.5 cm. deep and 4 cm. diameter. The sample was heated for 18 hr. at 105° in an oven. Each residue was then allowed to cool, and those oleoresins which produced opaque residues or residues too soft to be removed from the foil were regarded as defective. Volatile constituents were determined by this test using a 5 g. sample accurately weighed and heating in an oven at 105° to constant weight. Refractive indices

* Granted sabbatical leave from the Department of Pharmacognosy, School of Pharmacy, Brunswick Square, London, W.C.1.

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and acid values were obtained by the methods of the British Pharmacopoeia 1958. Constituents other than resin acids and volatile oil were determined in a defective sample by the following method. The oleoresin (100 g.) was heated at 105° to constant weight as above, and the soft, opaque residue was dissolved in ether (200 ml.). The resin acids were removed by washing with successive 25 ml. portions of sodium carbonate solution (5 per cent) until the addition of acetic acid to a sodium carbonate extract yielded no further precipitate. The bulked sodium carbonate extracts were washed with ether and the latter added to the original ether extract (A). The combined sodium carbonate extracts were acidified with acetic acid and extracted with ether. The dried ether extract on evaporation gave a solid residue which was weighed. The ether solution (A) was then washed with distilled water, dried over sodium sulphate and evaporated to give an oily residue. This was dissolved in light petroleum (b.p. 60–80°), and filtered to remove traces of insoluble "resene". Removal of solvent gave an oily residue, which was weighed. The refractive index of this oil was determined and an attempt made to saponify the oil using ethanolic potassium hydroxide.

Fresh Samples

These were obtained from four categories of trees. (i) Young trees 8–10 years old of average trunk diameter 10 cm. (ii) Old trees, 47 years old, of average trunk diameter 22 cm., (iii) dead and (iv) diseased trees. Random collections were made from different trees, giving bulk samples of approximately 200 ml. from each source. Acid values, percentage of volatile constituents and yields of resin were determined for each sample as described above.

RESULTS

Commercial Samples

The analytical figures (Table I) include results on oleoresins stored for six years (sample 56/9) and for two years (sample 60/3), also on oleoresins which gave a hard product on drying, and some on adulterated samples. Figures for refractive index were never outside the range 1.520 to 1.523 except for sample 61/2 which gave a result of 1.501. Analysis of this sample yielded resin acids 42.62 per cent and non-volatile

TABLE I
ANALYTICAL RESULTS* FOR COMMERCIAL SAMPLES

| Sample | Acid value of oleoresin | Volatile constituents per cent of oleoresin | Yield of resin per cent | Colour and condition of resin | Acid value of resin |
|--------|-------------------------|---|-------------------------|-------------------------------|---------------------|
| 60/3 | 73 | 28 | 72 | pale yellow, hard | 101 |
| 56/9 | 71 | 29 | 71 | pale yellow, hard | 100 |
| 61/1 | 66 | 25 | 75 | pale yellow, soft | — |
| 61/2 | 54 | 20 | 80 | opaque, soft | — |
| 61/3 | 67 | 24 | 76 | pale yellow, soft | — |
| 61/4 | 77 | 30 | 70 | dark red brown, hard | 110 |
| 62/1 | 71 | 24 | 76 | pale yellow, hard | 93 |
| 62/2 | 84 | 23 | 77 | pale yellow, hard | 109 |

* All based on duplicate determinations.

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oil 37.2 per cent. The oil was pale yellow in colour, almost odourless, could not be saponified with alcoholic potassium hydroxide and had a refractive index of 1.459. The resin acids were hard and reddish brown in colour.

When a mixture of good quality oleoresin and liquid paraffin B.P. (33 per cent) was heated at 105° it gave an opaque, soft product; liquid paraffin (5 per cent) gave a soft clear product, whilst one per cent produced a hard resin on drying.

Fresh Samples

The oleoresin from old, diseased and dead trees was thicker in consistency than that from young trees. Resin from young trees was pale yellow, that from diseased trees was cloudy and samples from dead trees were reddish brown. Analytical results are given in Table II.

TABLE II
ANALYTICAL RESULTS FOR FRESH SAMPLES

| Sample | Acid value of oleoresin | Volatile constituents per cent of oleoresin | Yield of resin per cent | Colour and condition of resin | Acid value of resin |
|----------------|-------------------------|---|-------------------------|-------------------------------|---------------------|
| Young trees | 73 | 25 | 75 | pale yellow, hard | 97 |
| Old trees | 91 | 24 | 76 | pale amber, hard | 120 |
| Diseased trees | 83 | 26 | 74 | pale amber, hard | 112 |
| Dead trees | 92 | 20 | 80 | reddish-brown, hard | 115 |

DISCUSSION

Commercial Samples

The screening test described (see p. 1) not only detects samples adulterated with mineral oils, but will also detect Oregon balsam derived from *Pseudotsuga taxifolia* which gives a soft resin when dried (Bender, 1951). Tests carried out with mixtures of liquid paraffin and oleoresin show that adulteration with 5 per cent mineral oil but not one per cent may be detected by this means. A sample of Canada balsam adulterated with a vegetable oil also gives a soft product after drying but the residue is never opaque and a high saponification value would give corroborative evidence of the presence of glycerides. The opacity of residues obtained from Canada Balsam heavily adulterated with mineral oil is explained by the insolubility of the "resene" in mineral oils: this constituent is consequently deposited when the volatile oil is removed. The "resene" is soluble in vegetable oils, hence the residue from a sample adulterated with such an oil is clear, not opaque. The occurrence of commercial oleoresin having an acid value as low as 54 is new. Previous adulteration was associated with acid values higher than 110 (Roberts and Becker, 1913), and this was due either to substitution with Oregon balsam or crude turpentine. Solvent extraction of sample 61/2 showed that this had been adulterated with what was probably a commercial petroleum oil. From the amount present in the sample, accidental contamination seems unlikely. Visits to the province of Quebec showed that accidental contamination of Canada balsam can easily occur. In place of standard,

clean receptacles, tins used for storing petrol, lubricating oil, heating or cooking oils are often used for collection.

The percentage of volatile constituents gave little indication of the quality of the commercial samples, although gross adulteration with turpentine would be detected by this method. Table I shows that oleoresins stored for several years in a tightly closed container (samples 56/9 and 60/3) are similar to fresh samples from young trees (Table II). The weight of residue after removing the volatile constituents indicates the yield of resin to be expected from good commercial samples only. For adulterated samples, e.g. 61/2, the higher weight of residue is misleading, due to the presence of a liquid non-volatile component. Only one sample (61/2 see p. 2) was shown to be unsatisfactory for optical purposes on the basis of refractive index.

Fresh Samples

Table II indicates a wide range of acid values for the fresh oleoresins: the colour of resin obtained from these samples varies from pale yellow to amber to reddish brown. Acid values of 80–90 (B.P.C. 1934) and 84–87 (Bender 1951) for Canada balsam have been reported, but in the present work, acid values of some good quality commercial samples were 71–77. (Table I). Oleoresins from young trees (8–10 years old) give a lower acid value than oleoresins from older trees (Table II), and in the Montmorency County of Quebec it is from such young trees that resins are obtained. In other regions of Canada where older trees remain, acid values of 80–90 would still be expected. Dead trees would yield acid values in the range 90–100. Since commercial material comprises bulked oleoresins from different sources, however, an average value would be expected. The acid value of Canada balsam also varies with changes in the amount of volatile oil, which is lower in samples from dead trees. Loss of volatile oil (which has an acid value, zero) through defective storage would also cause an apparent increase in acid value. This suggests that an acid value calculated on the basis of the resin content is a more reliable criterion of purity than one calculated in terms of the oleoresin. It is also evident that there would be less likelihood of adulteration of Canada balsam if it were exported and sold in the form of the resin, and this would also reduce transportation costs.

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