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Chapter III — Accroides

Gum accroides is the resinous product obtained from various members of the species *Xanthorrhoea* of the natural order *Juncaceae*, which occurs throughout Australia and Tasmania in red and yellow forms. The resin is also known as red gum, gum acaroid, grass tree gum, “Black Boy” gum, yacca or yacka gum, and Botany Bay resin. The last-named resin is relatively scarce. The yellow variety is the product of *Xanthorrhoea hastilis*. All other *Xanthorrhoea* trees yield the red resin. The

bulk, of commercial red gum is obtained from South Australia and Kangaroo Island and is the product of *Xanthorrhoea tateana*.^[1]

The *Xanthorrhoea* trees grow slowly and usually attain a height of 7 or 8 feet before branching into a tuft of rushlike leaves about 3 feet in length. The trunks are composed of a fibrous, pithy material surrounded by a jacket approximately 3-inches thick formed by the dying off of old rushlike leaves. The charring of this leafy jacket during forest fires leads to the name of “Black Boy”.

The resin accumulates at the base of the dead leaves along the stem and is collected by stripping the enveloping husk from the core with an axe. Occasionally the husk may be sufficiently soft to permit easy removal, but more frequently, it is a hard coherent mass, which must be me-

chanically separated from the core. The proportion of resinous husk to the core, which varies with the season, is less in winter than in summer.^[2] The cut should not be made directly to the core of the tree, as the leaf bases are then cemented together in large blocks that are subsequently rejected in the sieving operation. On the other hand, when a series of shallow cuts are made, the leafy bases are sufficiently reduced in size to make separation from the resin difficult. The cutting requires considerable skill and should be to such a depth that the leaf bases separate readily. Chopping off the crown of the tree is the customary, though unnecessary, practice. When the crown of the tree is uncut, removal of the husk seems to have little effect upon the tree, provided that sufficient resin is left to protect the core. Even when "lopped", the tree frequently recovers. The husks fall into frameworks placed about the base of the tree. They are then collected and subjected to a sieving operation in a "jigger", which removes most of the leaf bases and any large lumps of caked husk, as well as separates the resin into two grades. The jigger consists of an inclined sieve of wire netting (1/2 to 3/4-in. mesh) above an inclined metal sheet containing smaller perforations. A horizontal shaking motion is imparted to the gratings while the husks are fed in through a hopper at the top. A winnowing operation separates any leaf bases remaining with the coarse gum.^[3]

The collection of accroides is subject to licensing according to the district in which the resin is to be collected. The quantity of resin obtainable from an individual tree appears to vary with the species from which collected, and possibly with other factors. Estimates of different collectors vary from 2 to 4 pounds or lower to upwards of 40 or 60 pounds.^[4,5,6] A similar situation is met with the amount of resin collected per man per day. Estimates range from 25 to 100 pounds.

The sieving and winnowing method of purifying accroides is subject to high losses of resin. Methods designed to avoid these losses have been studied. A procedure in which the mixed gum and leaf bases are placed on sieves in a steam-heated vat has been in commercial operation. The molten resin runs into trays and is later removed to cooling receptacles. Resi-

due from the screens is utilized as fuel. The product contains but little foreign matter and the yield of resin is increased by one-third over the jigger process, but the tree dies as the result of the lopping and stripping operations employed. The slow growth of the tree, however, makes it desirable that collection methods should not result in its destruction. Solvent extraction methods^[7] have also been employed for the purification of accroides. Patents^[8] have been granted for a method of purification in which the resin is dissolved in a dilute alkaline solution, filtered, and then precipitated with acid. By proper control of the temperature during precipitation, the resin is obtained in a granular condition, which can be easily handled.

Approximately seventeen varieties of the tree are known, but commercial distinction is made only between the yellow and the more prevalent red gum. The gradings of accroides are according to color, particle size, and material, which is produced as a result of screening, with the commercial grades yellow, red gum coarse, and red gum powdered. The red gum is usually in the form of small dusty pieces of a reddish brown color, which is exported in bags of 140 pounds.

Accroides differs from the other natural varnish resins in that it contains appreciable quantities of free benzoic and cinnamic acids and is thus closely related to the balsams. The resin is of the alcohol-soluble type and is insoluble in aryl and aliphatic hydrocarbons. Like the manilas, both varieties are soluble in alkali. The alcohol solution of red accroides gradually deposits benzoic acid upon standing. The yellow variety also contains benzoic acid obtainable by acidifying the alcohol solution with hydrochloric acid.

The composition of yellow and red accroides has been studied by a number of investigators. The results obtained are listed in Table 3. Both varieties contain a resin-tannol, which yields picric acid upon nitration. The yield, which varies according to the species of *Xanthorrhoea* from which the resin is obtained, is of the order of 50% for the yellow and from 5 to 50% for the red variety.^[9] A number of processes have been suggested, and the preparation of picric acid and nitrophenols from accroides has been patented.^[10] Small yields and high nitric acid consumption do not permit economic competition with chemical production of picric acid from

Table 3. Chemical Composition of Accroides

Constituent	Formula	Basicity	Percent	Remarks
<i>p</i> -Coumaric acid Free ^[a]	HOC ₆ H ₄ CH:CHCOOH (<i>p</i> -oxycinnamic acid)	Mono	1	These results are for red accroides, the characteristic resinotannol of which is erythroresinotannol, C ₄₀ H ₃₉ O ₉ OH
Combined with benzoic and cinnamic acids and a tannol ^[a]			2	
<i>p</i> -Oxybenzaldehyde ^[a]		0.6		
Resinotannol ^[a]		85		
<i>p</i> -Coumaric acid Free ^[a]	HOC ₆ H ₄ CH:CHCOOH (<i>p</i> -oxycinnamic acid)		4	
Combined with tannol ^[a]			7	
Cinnamic acid Free ^[a]	C ₆ H ₅ CH:CHCOOH		0.5	
Combined with tannol ^[a]			0.6	
Styracin and probably the phenyl propyl ester of cinnamic acid ^[a]			1	
<i>p</i> -Oxybenzaldehyde and probably vanillin ^[a]			0.6	
Resinotannol ^[b]			80	
<i>p</i> -Coumaric acid Free ^[b]	HOC ₆ H ₄ CH:CHCOOH (<i>p</i> -oxycinnamic acid)	Mono	0.5	
Combined ^[b]			1.5	
Cinnamic acid ^[b]	C ₆ H ₅ CH:CHCOOH	Mono	0.1	
Styracin ^[b]			0.1	

[a] A. Tschirch and K. Hildebrand, *Arch. Pharm.*, **234**, 698 (1896).

[b] *Bull. Imp. Inst.*, **18**, 155 (1920).

See also: Nagai, *Ber.* **24**, 2847 (1891); E. H. Rennie, W. T. Cook, and H. H. Finlayson, *Trans Chem. Soc.*, **117**, 338 (1920); H. H. Finlayson, *J. Chem. Soc.*, 2763 (1926).

phenol or chlorobenzene. The belief has been expressed, however, that appreciable quantities of accroides were utilized for the preparation of explosives by Germany during the First World War.

The constituents of accroides are also suitable as the starting point in the synthesis of certain organic dyestuffs. Treatment with sulfuric acid or with sulfur in the presence of an alkali has been patented^[11] as a means of producing brown and black dyes.

Attempts to bleach accroides in a manner similar to shellac have been unsuccessful. Simion^[12] reported the bleaching of red accroides in acid solution but found that the color

returned upon standing. His alcoholic solution of the yellow resin gradually darkened to the color of the red gum solution when exposed to air. Gardner and Parkes^[13] applied the usual hypochlorite method for bleaching shellac to accroides but did not obtain satisfactory results.

Penfold^[14] studied the removal of coloring matter and insolubles from accroides by solvent extraction methods. He found that use of benzol as the solvent in a modified Scott extraction plant yielded a superior resin containing much less coloring matter and tannins than the crude resin. The product was stated to be directly applicable to the resin industry without need for further bleaching or refining. The purified resin may be bleached directly with chlorine or in so-

lution by the use of peroxides. The bleached resin is stated to be suitable for the manufacture of sealing wax and pale ester gums. It was also reported that the process involved very low costs for fuel, power, and labor and that solvent losses were less than 1 percent of the charge treated.

Accroides differs markedly from the other natural resins in that it is the only material, which, as marketed, is heat-reactive in a manner analogous to that of the heat-reactive phenol-formaldehyde resins. When heated to thermal processing temperatures, the resin is converted into hard, completely insoluble, and unusually resistant films. Manila and Congo copals possess similar properties under specific conditions, but not in the form in which they are marketed. Owing to its heat-reactive properties, accroides is not adapted to the preparation of oil varnishes. Accroides is compatible with cellulose acetate and cellulose nitrate, but not with ethyl cellulose.

The low price and heat-reactive properties of accroides have a definite influence upon its commercial use. One application is as a binder in the preparation of wallboard. It is a substitute for rosin in paper coating and for shellac in spirit varnishes, lacquers, and printing inks. The resin is also used in the preparation of finishes for cellulosic materials, metals, metal foil, and glass as well as in the preparation of molding powders from phenol-formaldehyde resins.^[15] Livache and McIntosh^[16] mention concentrated solutions of red accroides plasticized with castor oil or balsam as a red coating for windows of photographic laboratories to exclude the active rays of the sun.

References

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