Neutrals in Southern Pine Tall Oil

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ABSTRACT

Black-liquor soap skimmings from commercial pulping of southern pine wood contained 4.8% neutrals by wt. The neutrals were quantitatively analyzed and more than 80 compounds found. All of the compounds that comprised 0.1% or more of the neutrals were identified; these included 0.3% α-terpineol, 2.5% diterpene hydrocarbons, 8.1% resin alcohols, 10.0% resin aldehydes, 0.5% resin acid methyl esters, 1.2% norditerpene alcohols, 16.8% labdane diterpenes, 2.1% other diterpenes, 32.4% steroids, 0.6% triterpenes, 0.7% polyprenols, 6.1% wax alcohols, 5.7% stilbenes, 4.4% lubricating oil, and 8.6% minor (<0.1%) constituents. Sitosterol, campesterol, stigmastanol, pinosylvin dimethyl ether, lignoceryl and ceryl alcohols, agathadiol, isoagatholal, communol, abietal, and diterpenes with the pimarane or isopimarane skeleton were the major components.

INTRODUCTION

After concentrating the black colored liquor remaining from kraft (sulfate) pulping of conifer wood chips, a semisolid soap is salted out that is skimmed off and acidified to yield crude tall oil. Tall oil is a complex mixture of 40-60% fatty acids, 40-55% resin acids, and 5-10% neutral components (1,2).

The neutral constituents have no commercial value. Increased information on tall oil neutrals could lead to new products and improved utilization of tall oil fatty and resin acids. These neutrals also cause losses of the fatty and resin acids during refining of crude tall oil due to esterification. During distillation of crude tall oil, the neutral components also contaminate the resin and fatty acid fractions and the distilled tall oil, and are major components in the forerun and the pitch. For example, tall oil heads contain 25-60% neutrals, tall oil fatty acids, 1-10% neutrals, tall oil rosin, 3-7% neutrals, and tall oil pitch, 20-35% neutrals. However, part of these neutrals are artifacts of the distillation process.

Southern pines (pines growing in the southeastern US) are the major domestic source of pulpwood and tall oil. Although the extracts of *Pinus* spp., especially the oleoresinous exudates and the heartwood phenolics, have been investigated in some detail, the neutral components from southern pines have not. Sandermann and Weissmann (3) have studied the neutrals from American tall oil heads, and Joye, et al., (4) have carried out a cursory gas liquid chromatography (GLC) analysis of the neutrals from gum, wood, and tall oil rosin. The neutrals in European (5,6) and Canadian (7-9) tall oils have been studied. A detailed analysis of the neutral components in a pooled sample of black-liquor soaps from several mills pulping 100% southern pine is reported here.

EXPERIMENTAL PROCEDURES

Melting points were measured in evacuated capillaries, and were corrected. Optical rotations were obtained in $CHCl_3$ (c1). All percentages of individual compounds were obtained from GLC analysis by normalization of peak areas.

Extraction of Black Liquor Soap Skimmings

A combined sample of black-liquor soap skimmings (9267 g) from commercial pulping of southern pine wood was dissolved in benzene:methanol (1:1). Portions were added to a large volume of dilute NaOH and continuously extracted with diethyl ether:benzene. The combined extracts contained residual acidic components which were removed slowly and incompletely by exhaustive washings with dilute NaOH. The extract was concentrated, acidified, washed with water to neutral pH, diluted with diethyl ether:methanol (9:1), and passed through excess DEAE-Sephadex (10) to remove completely these residual acids. This yielded 449 g of neutrals (4.8% of the soap skimmings).

Fractionation of Neutrals

Crystallization of the neutrals several times alternately from methanol and from heptane yielded a crystalline fraction (111 g) and an oily fraction (338 g). Each fraction was analyzed separately.

The crystalline fraction was a relatively simple mixture that contained the bulk of the sterols, wax alcohols, and triterpenes. The wax alcohols were separated from the crystalline fraction via the urea canal inclusion complex (11). The 3β-hydroxysterols were isolated from this fraction as the digitonides, which were subsequently cleaved by dimethyl sulfoxide (12). The remainder of the fraction was the triterpenes. The oily fraction was a complex mixture of diterpenes, stilbenes, polyprenols, steroids, and lubricating oil.

The carbonyl components were separated from a portion of the oily fraction as their Girard hydrazones (13) using Amberlite IRC-50 as the acid catalyst (14). The hydrazones were cleaved with dilute sulfuric acid. Girardation was used only as a qualitative method for separating and identifying the carbonyl components. These components were subsequently re-isolated and quantitated on fractionating the oily fraction by the methods below.

The remaining 3β-hydroxysterols were isolated from the oily fraction as the digitonides, and were cleaved as before. The sterol free oily fraction was chromatographed over silica gel (40X). This column was eluted with petroleum ether (PE), PE:benzene mixtures, benzene, and then benzene:methanol mixtures. PE eluted the lubricating oil. PE: benzene eluted the following fractions: a) the diterpene hydrocarbons; b) a mixture of diterpene hydrocarbons and squalene; c) a mixture of 8-epimanoyl oxide and pimaral; d) a mixture of resin aldehydes; and, finally, e) a mixture of resin aldehydes and resin acid methyl esters. Benzene eluted the following fractions: a) methyl dehydroabietate; b) *cis*- and *trans*-pinosylvin dimethyl ether, c) a mixture containing *trans*-pinosylvin dimethyl ether, 3,5-stigmastadien-7-one, 3,5-campestadien-7-one, resin alcohols, manool, 13-epimanool, 15,16-dinorlabd-8(17)-en-13-one, cycloartenol, and 24-methylenecycloartanol; and, finally, d) a mixture of wax alcohols, resin alcohols, *trans*-communol, 18-norditerpene alcohols, 8(17),*E*-13-labdadien-15-ol, and geranylgeraniol. Benzene:methanol eluted the following fractions: a) a mixture of wax alcohols; 18-norditerpene alcohols, geranylgeraniol, 9,10-secodehydroabietan-18,10-olide, hydroxymanool oxide, 4-campesten-3-one, 4-stigmasten-3-one, 4,6-campestadien-3-one, 4,6-stigmastadien-3-one, α-terpineol, and an unknown serratene aldehyde; b) isoagatholal; c) 19-hydroxy-15,16-dinorlabd-8(17)-en-13-one; d) agathadiol; and, finally, e) a mixture of agathadiol, 8(14),15-pimaradiene-3β,18-diol, and 8,11,13-abietatriene-15,18-diol.

The individual fractions obtained from the crystalline and oily fractions were routinely analyzed by thin layer chromatography (TLC) and GLC. These fractions were frac-

TABLE I

Composition of Southern Pine Tall Oil Neutrals

Compound[1]	%
Monoterpene	0.3
α-Terpineol^{a,b,d,f,g}	0.3
Diterpenes	41.2
Hydrocarbons	2.5
Pimaradiene^{d,e,h}	0.7
Sandaracopimaradiene^{d,e,h}	0.1
Isopimaradiene^{d,e,h}	1.0
Abietadiene^{c,d,e,h}	0.4
Dehydroabietane^{d,e,h}	0.2
Neoabietadiene^{d,e}	0.1
Resin alcohols	8.1
Pimarol$^{a',b',d,d',e,g',h',j}$	3.3
Sandaracopimarol$^{a',d,d',e,g',h',j}$	0.3
Isopimarol$^{a',b',d,d',e,g',h',j}$	3.6
Abietol^{d,e,j}	0.5
Dehydroabietol^{d,e,j}	0.3
Neoabietol^{d,e,j}	0.1
Resin aldehydes	10.0
Pimaral^{a,b,d,e,g,h}	3.1
Sandaracopimaral^{d,e}	0.2
Isopimaral^{a,b,d,e,g,h}	3.7
Abietal^{a,b,c,d,e} (mp = 45-47 C)	1.7
Palustral/levopimaral^{d,e}	0.1
Dehydroabietal^{a,b,d,e,g,h}	0.9
Neoabietal^{d,e}	0.3
Resin acid methyl esters	0.5
Methyl pimarate^{d,e,g,h}	Trace
Methyl sandaracopimarate^{d,e}	Trace
Methyl isopimarate^{d,e,g,h}	0.1
Methyl abietate^{d,e}	Trace
Methyl dehydroabietate^{a,b,d,e,g,h}	0.4
Norditerpene alcohols	1.2
18-Norpimarol^{d,e,f,h,j}	0.2
18-Norsandaracopimarol^{d,f,j}	Trace
18-Norisopimarol^{d,e,f,h,j}	0.4
18-Norabietol^{d,f,j}	0.3
18-Nordehydroabietol^{d,f,j}	0.3
Labdanes	16.8
Manool$^{a,a',b,b',d,f,g',h,i',\ell'}$	0.2
13-Epimanool$^{a',i',\ell'}$	0.1
trans-Communol$^{a',b',c,c',d,e',g,h'}$	3.7
trans-Communal^{d,e}	0.3
Agathadiol$^{a,b,d,d',e',f,f',g}$	6.4
Isoagatholal$^{a,a',b,b',g',i'}$	4.4
8(17),*E*-13-Labdadien-15-ol$^{a',b',d',e',g',h'}$	0.3
8-Epimanoyl oxide$^{a,b,c,\ell}$ (mp = 44-44.5 C, $[\alpha]_D^{25}$ - 9.6°)	0.7
Hydroxymanool oxide[2]	0.2
15,16-Dinorlabd-8(17)-en-13-one^{a,b,d,e,g,h}	0.1
19-Hydroxy-15,16-dinorlabd-8(17)-en-13-one[2]	0.4
Other	2.1
Geranylgeraniol$^{a,a',b,d,f,g}$	0.9
8(14),15-Pimaradiene-3β,18-diol[2] (mp = 179.5-180.5 C, $[\alpha]_D^{25}$ + 93°)	0.5
9,10-Secodehydroabietan-18,10-olide[2]	0.6
8,11,13-Abietatriene-15,18-diol[2]	0.1
Steroids	32.4
Cholesterol^{d,f}	Trace
Campesterol$^{d,d',f,f'}$	2.5
Campestanol$^{f'}$	0.3
Sitosterol$^{a,a',b,b',d,d',f,f',g,g'}$	25.1
Stigmastanol$^{a',b',f',g',h',i',\ell'}$	1.9
Cycloartenol$^{a',b',d,d',g',h'}$	0.5
24-Methylenecycloartanol$^{a',b',d,d',g',h'}$	0.8
24-Methylenelophenol$^{a',b',f',g',h'}$	Trace
Citrostadienol$^{a',b',d,d',f',g',h',\ell'}$	0.2
Obtusifoliol$^{d,d',f,f'}$	0.1
Cycloeucalenol$^{d,d',f,f'}$	0.1
4-Stigmasten-3-one^{a,b,c,d,f,g,h}	0.2
4-Campesten-3-one^{d,f}	Trace
4,6-Stigmastadien-3-one^{c,d,f}	0.1
4,6-Campestadien-3-one^{d,f}	Trace
3,5-Stigmastadien-7-one^{a,b,c,d,g,h,i}	0.5
3-5-Campestadien-7-one^{d}	0.1
Triterpenes	0.6
Squalene^{a,b,d,f,g}	0.2
Serratenediol^{a,b,d,g,i}	0.1
21-Episerratenediol^{a,b,d,g,i}	0.1
3β-Hydroxy-14-serraten-21-one^{a,b,d,g,i}	Trace
Unknown serratene aldehyde	0.2
Polyprenols^{a}	0.7
Wax Alcohols	6.1
1-Hexadecanol (cetyl alcohol)$^{a',d'}$	Trace
1-Octadecanol (stearyl alcohol)$^{a',d'}$	Trace
1-Eicosanol (arachidyl alcohol)$^{a',d'}$	0.3
1-Heneicosanol$^{a',d'}$	Trace
1-Docosanol (behenyl alcohol)^{a,b,d,g,k}	0.8
1-Tricosanol^{a,b,d,g,k}	Trace
1-Tetracosanol (lignoceryl alcohol)^{a,b,d,g,k}	3.7
1-Pentacosanol^{a,b,d,g,k}	Trace
1-Hexacosanol (ceryl alcohol)^{a,b,d,g,k}	1.3
1-Octacosanol (montanyl alcohol)^{a,b,d,g,k}	Trace
Stilbenes	5.7
trans-Pinosylvin dimethyl ether^{a,b,c,d,g,i}	5.6
cis-Pinosylvin dimethyl ether^{d}	0.1
Minor Constituents (<0.1% each)	8.6
Lubricating Oil^{a,b,d,k}	4.4

[1] Methods of identification are indicated for each compound as follows: a, NMR; b, IR; c, UV; d, gas liquid chromatography (GLC) on SE-30 or SE-30/EGiP; e, GLC on DEGS; f, GLC on other liquid phase(s); g, thin layer chromatography (TLC) on SiO_2; h, TLC on $AgNO_3/Al_2O_3$ (SiO_2); i, minimum mp; j, near IR; k, tetranitromethane; ℓ, optical rotation. All letters with prime sign refer to a derivative of the compound.

[2] New natural product, the structure of which will be discussed in a forthcoming paper.

tionated further by rechromatography on silica, $AgNO_3$-silica, alumina, or $AgNO_3$-alumina (15,16) and by preparative GLC, distillation, or crystallization of the product or a suitable derivative. Numerous chromatograms were required for further fractionation, and often the same component was obtained from different chromatograms.

The individual components were then identified by comparing with authentic reference compounds or reference data by one or more of the following methods as indicated in Table I: Nuclear magnetic resonance (NMR), infrared (IR), ultraviolet (UV), TLC (silica, $AgNO_3$-silica), GLC (SE-30, DEGS, OV-17, PPE-20), optical rotation, mp, and mixture mp. The proof of structure for the 5 new natural products will be published separately.

RESULTS AND DISCUSSION

The methods used for the fractionation of the neutrals are, except for minor changes, the methods successfully used in this laboratory to study pine bark terpenoids (17-22). In some cases, these methods yielded mixtures of related compounds, e.g., the wax alcohols, which were analyzed as a group without further fractionation. The analysis of the tall oil neutrals is presented in Table I, which includes the individual compounds and the methods used for

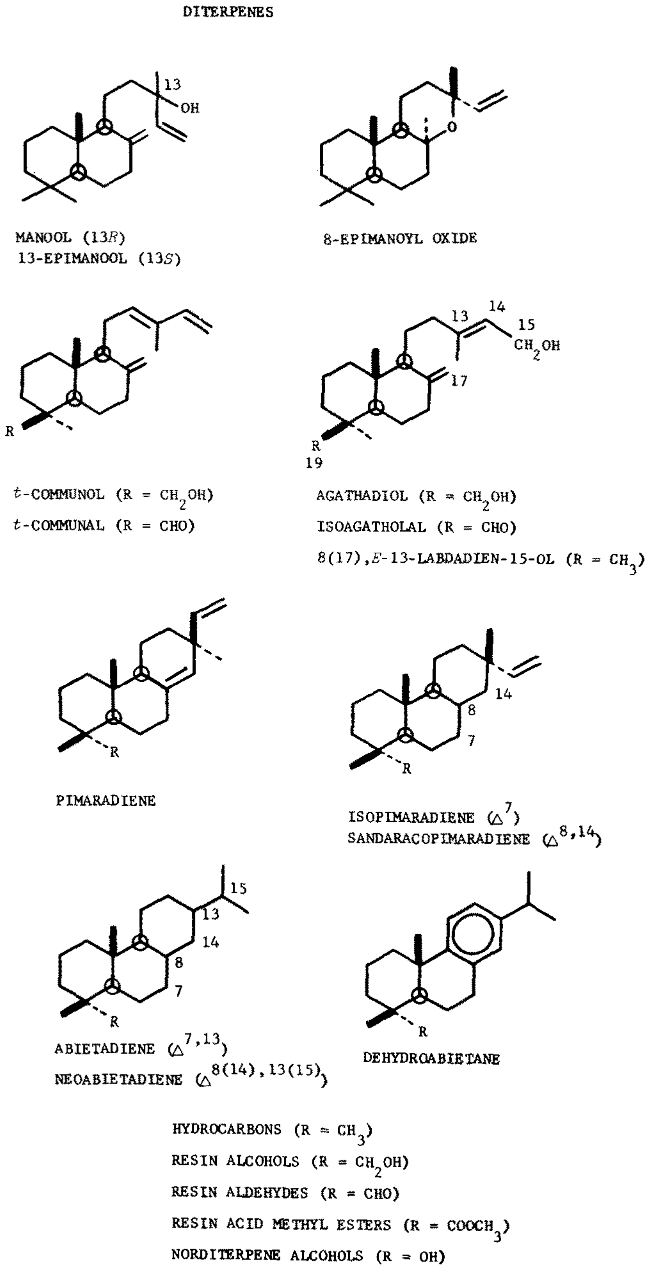

FIG. 1. Diterpenes in southern pine tall oil.

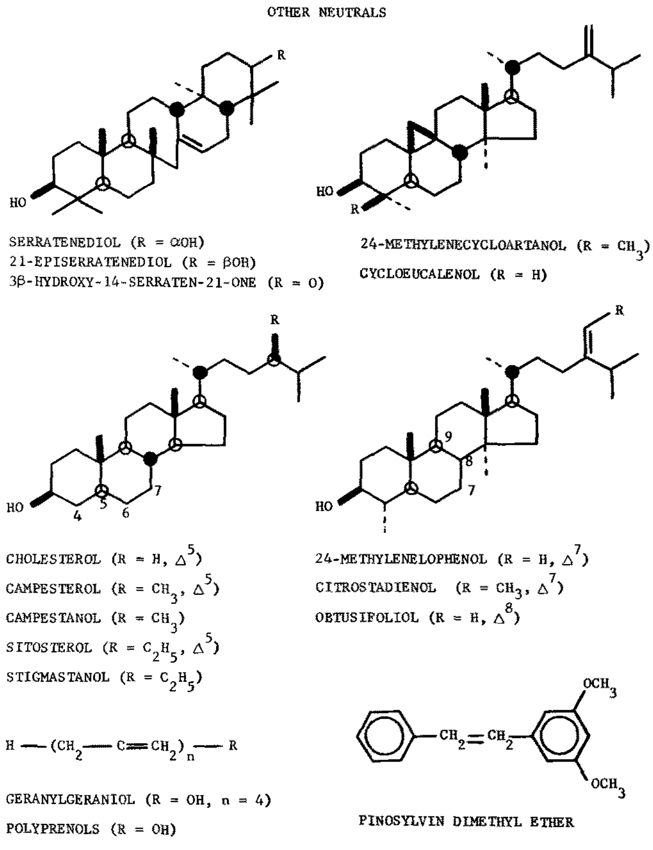

FIG. 2. Triterpenes, steroids, and other neutrals in southern pine tall oil.

their identification. Because the composition of commercial tall oils varies, all the neutral components of 0.1% or more were examined to ensure the identification of all of the major neutrals in any southern pine tall oil.

The diterpenes in tall oil are based on the pimarane, isopimarane, abietane, and labdane skeletons (Fig. 1) analogous to the known resin acids. Geranylgeraniol is generally recognized as the biogenetic precursor of the diterpenes. It is widely distributed in plants and has been reported from *Pinus sylvestris* and tall oil (5,23). The diterpene hydrocarbons have been reported from several pines (4,17,18,24-32). The resin alcohols (4,18,25,26,28,30,32-40) and the resin aldehydes (25,26,31,32,35,36,41-45) are widely distributed in *Pinus* spp., and have been reported in tall oil (3,4,6-9). Neoabietadiene and sandaracopimaral have not been previously reported in *Pinus* spp.

Several 18- and 19-norditerpene alcohols recently have been reported from the pines (17,18,30,37,46-48), but not from tall oil. Several publications (49-54) question whether norditerpene alcohols are natural products or are formed by autoxidation of the corresponding aldehydes. Axial (C-19) aldehydes apparently autoxidize more readily than the equatorial (C-18) aldehydes. The 18-norditerpene alcohols from tall oil probably are formed by autoxidation, most likely during chip storage and pulping of trace amounts of the corresponding C-19 aldehydes or of the more common C-18 aldehydes. Therefore, traces of 19-norditerpene alcohols and norditerpene olefins in the tall oil neutrals are to be expected, although their presence was not proved conclusively.

Although the neutrals were at times dissolved in methanol, care was taken to avoid conditions that could lead to esterification, e.g., the formation of resin acid methyl esters. Naturally occurring methyl pimarate, isopimarate, sandaracopimarate, palustrate/levopimarate, dehydroabietate, abietate, and neoabietate have been reported in the Pinaceae (27,32,37,38,55).

The labdane compounds are a major fraction of the tall oil neutrals. Isoagatholal (contortolal) was first isolated from *Pinus contorta* bark (17,56). It has been reported since in *P. koraiensis* oleoresin (46) and *Cupressus sempervirens* (57). Agathadiol (contortadiol), also first reported as a natural product in *P. contorta* bark (19,56), has been reported in other *Pinus* spp. (19,38,58-61). 15,16-Dinorlabd-8(17)-en-13-one has been found in *P. monticola* bark (37) and in *Dacrydium kirkii* (62). The related compound 19-hydroxy-15,16-dinorlabd-8(17)-en-13-one has been found in *P. banksiana* bark (18). 8(17),*E*-13-Labdadien-15-ol is a known natural product reported in *P. banksiana* (18), *P. pumila* (63), *Larix sibirica* (64), and *D. kirkii* (62). *trans*-Communol (elliotinol) was first reported in *P. elliottii* (40), and has been reported since in tall oil (4), in *P. quadrifolia* (30), and in *Agathis australis* (65). 8-Epimanoyl oxide has been found only in *Chamaecyparis nootkatensis* (66,67). Surprisingly, the well known epimers of this compound, manoyl oxide and 13-epimanoyl oxide (68), were not detected among the tall oil neutrals.

Manool and its 13-epimer are of widespread occurrence

(68). Although 13-epimanool is common to the Pinaceae, manool has never been reported in this family. Manool or 13-epimanool or both have been reported from Canadian tall oil (7-9). Although these epimers are difficult to distinguish by spectral and physical means (56), they can be distinguished as the 3,5-dinitrobenzoates (DNB). The pure mixture from tall oil could not be crystallized, buts its DNB was crystallized alternately from methanol and from hexane to constant mp = 94.5-96.5 C, $[\alpha]_D^{24} + 14°$. The mp was undepressed on admixture with authentic manool DNB, mp = 103.5-104.5 C, $[\alpha]_D^{24} + 8°$, but was depressed on admixture with authentic 13-epimanool DNB, mp = 119-121 C dec., $[\alpha]_D^{22} + 33°$. It was identical to manool: epimanool DNB by NMR, IR, and TLC. These data, especially the optical rotation and mp, indicate that the isolated compound is a mixture of ca. 75% manool and 25% 13-epimanool. This has been confirmed by the NMR spectra of the free alcohols (69, Conner and Rowe, unpublished data).

Cycloartenol, 24-methylenecycloartanol, cycloeucalenol, obtusifoliol, 24-methylenelophenol, and citrostadienol (24-ethylidenelophenol) (Fig. 2), which are all present in small amounts in the tall oil neutrals, are among the compounds postulated as intermediates in the conversion of squalene to sitosterol (70). Cycloartenol and 24-methylenecycloartanol, which are widely distributed in higher plants (70), have been reported in *Pinus sylvestris* (5,32) and *P. elliottii* (71). 24-Methylenecycloartanol has also been isolated from *P. monticola* bark (37). Cycloeucalenol, 24-methylenelophenol, and obtusifoliol are now recognized as common trace sterols in plants (70), but have not been reported in the Pinaceae. Citrostadienol (72), which has been found in *P. sylvestris* (5,32,51), is a common component of higher plants (70), and probably is accompanied invariably by trace amounts of 24-methylenelophenol (73,74).

4-Stigmasten-3-one, 4,6-stigmastadien-3-one, and 3,5-stigmastadien-7-one may be merely autoxidation products of sitosterol. They occur admixed with lesser amounts of the corresponding campestane derivatives, analogous to the occurence of campesterol in isolations of sitosterol.

Stigmastanol is normally present in most sitosterol isolations (75), and occurs with lesser amounts of campestanol. The dehydrosterols in the neutrals were separated quantitatively by chromatography of the crude sitosterol acetate on $AgNO_3$-silica. This method is preferred to the usual method of analysis for the dihydrosterols by acetylation and oxidation (73,75).

Serratene derivatives have been reported in bark of various *Pinus* and *Picae* species (17,20,21,27,28,37,76-79). Indeed, serratenediol was first found in *Pinus banksiana* bark (21,78). No further work is planned on the serratene aldehyde due to decomposition of the isolated sample, probably by autoxidation of a tertiary aldehyde (49-54).

Pinosylvin dimethyl ether is common to the pines as are the wax alcohols (22). Polyprenols have been reported in higher plants (80-84), in birch tall oil (5), in *Pinus strobus* (79), and in *Larix decidua* (85). Although most polyprenols isolated contain 6-13 isoprenoid units, the polyprenols found in the tall oil neutrals contain ca. 18 isoprenoid units (by integration of the NMR spectrum) analogous to those found in *P. strobus* and *L. decidua*. Pinoprenol acetates and piceaprenol acetates (10-19 isoprenoid units) have been isolated from *P. sylvestris* needles and *Picea abies* needles, respectively, but were not detected in the wood (86).

As expected, the tall oil neutrals are similar to the neutrals obtained on extraction of pine wood. Sterols and diterpenes comprise the major neutral components. Sitosterol is the major sterol and, indeed, the major single compound. The major diterpenes are the labdanes, resin aldehydes, and resin alcohols.

ACKNOWLEDGMENTS

M. Jaeger isolated *trans*-communol, 8(17),*E*-13-labdadien-15-ol, and geranylgeraniol from the neutrals; G. Ourisson provided a sample of cycloeucalenol; A.G. Gonzalez, a sample of obtusifoliol; O. Jeger, a sample of 15,16-dinorlabd-8(17)-en-13-one; and E. von Rudloff furnished NMR and IR spectra of 8-epimanoyl oxide. Black-liquor soap skimmins were provided by St. Regis Paper Company, Jacksonville, FL, Westvaco Corp., North Charleston, SC, and Arizona Chemical Company, Panama City, FL.

REFERENCES

1. Zachary, L.G., H.W. Bajak, and F.J. Eveline, Editors, "Tall Oil and Its Uses," F.W. Dodge Co., New York, N.Y., 1965, p. 12.
2. Zinkel, D.F., Chem. Tech. 5:235 (1975).
3. Sandermann, W., and G. Weissmann, Pap. Puu 44:639,643 (1962).
4. Joye, N.M., Jr., A.T. Proveaux, and R.V. Lawrence, JAOCS 50:104 (1973).
5. Holmborn, B., and E. Avela, Acta Acad. Abo. (Series B) 31:16 (1971).
6. Lundquist, A., and T. Kautto, Acta Chem. Scand. 20:1166 (1966).
7. Mitchell, D.L., Symposium on Chemistry of Tall Oil and Turpentine, 153rd ACS National Meeting, Miami, April, 1967, D-16.
8. Mitchell, D.L., Third Canadian Wood Symposium, Vancouver, BC, 1970, p. 17.
9. Mitchell, D.L., and M.S. Patel, "Unsaponifiable Constituents in Three Canadian Tall Oils," Product Research and Development Research Council, Alberta, Edmonton, Alberta, 1970.
10. Zinkel, D.F., and J.W. Rowe, Anal. Chem. 36:1160 (1964).
11. Schlenk, H., and R.T. Holman, J. Amer. Chem. Soc. 72:5001 (1950).
12. Issidorides, C.H., I. Kitagawa, and E. Mosettig, J. Org. Chem. 27:4693 (1962).
13. Wheeler, O.H., Chem. Rev. 62:205 (1962).
14. Teitelbaum, C.L., J. Org. Chem. 23:646 (1958).
15. Zinkel, D.F., and J.W. Rowe, J. Chromatogr. 13:74 (1964).
16. Norin, T., and L. Westfelt, Acta Chem. Scand. 17:1828 (1963).
17. Rowe, J.W., R.C. Ronald, and B.A. Nagasampagi, Phytochemistry 11:365 (1972).
18. Rowe, J.W., B.A. Nagasampagi, A.W. Burgstahler, and J.W. Fitzsimmons, Ibid. 10:1647 (1971).
19. Rowe, J.W., and G.W. Shaffer, Tetrahedron Lett. 2528 (1967).
20. Bower, C.L., and J.W. Rowe, Phytochemistry 6:151 (1967).
21. Rowe, J.W., and C.L. Bower, Tetrahedron Lett. 2745 (1965).
22. Rowe, J.W., C.L. Bower, and E.R. Wagner, Phytochemistry 8:235 (1969).
23. Dickhart, W., Amer. J. Pharmacy 127:359 (1955).
24. Vlad, P.F., and A.G. Russo, Aktual. Probl. Izuch. Efirnomaslich. Rast. Efirn. Masel 155 (1970).
25. Westfelt, L., Acta Chem. Scand. 20:2829 (1966).
26. Westfelt, L., Bull. Nat. Inst. Sci. India 37:105 (1968).
27. Norin, T., and B. Winell, Acta Chem. Scand. 26:2289 (1972).
28. Norin, T., and B. Winell, Ibid. 26:2297 (1972).
29. Vlad, P.F., A.G. Russo, M.N. Koltsa, and V.N. Paukov, Khim. Prir. Soedin. 7:20 (1971).
30. Zinkel, D.F., and A.H. Conner, Phytochemistry 12:938 (1973).
31. Hannus, K., and G. Pensar, Pap. Puu. 7:1 (1973).
32. Manell, D., and G. Pensar, Suom. Kemistiseuran Tiedonantoja 81:103 (1972).
33. Grant, P.K., C. Huntrakul, and D.R.J. Sheppard, Aust. J. Chem. 20:969 (1967).
34. Quon, H.H., and E.P. Swan, Can. J. Chem. 47:4389 (1969).
35. Shmidt, E.N., and V.A. Pentegova, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk 144 (1968).
36. Erdtman, H., and L. Westfelt, Acta Chem. Scand. 17:1826 (1963).
37. Nagasampagi, B.A., J.K. Toda, A.H. Conner, and J.W. Rowe, 161st ACS National Meeting, Los Angeles, March, 1971, paper 84.
38. Raldugin, V.A., N.K. Kashtanova, and V.A. Pentegova, Khim. Prir. Soedin. 6:481 (1970).
39. Baldwin, D.E., V.M. Loeblick, and R.V. Lawrence, J. Org. Chem. 23:25 (1958).
40. Joye, N.M., Jr., E.M. Roberts, R.V. Lawrence, L.J. Gough, M.D. Soffer, and O. Korman, Ibid. 30:429 (1965).
41. Sorensen, N.A., and T. Brunn, Acta Chem. Scand. 1:112 (1947).
42. Roberts, E.M., and R.V. Lawrence, J. Amer. Chem. Soc. 78:4087 (1956).
43. Russo, A.G., P.F. Vlad, and Lazur'evskii, Khim. Prir. Soedin. 4:193 (1968).
44. Harris, G.C., and T.F. Sanderson, J. Amer. Chem. Soc. 70:3870 (1948).
45. Lisina, A.I., and V.A. Pentegova, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk. 96 (1965).

46. Raldugin, V.A., and V.A. Pentegova, Khim. Prir. Soedin. 7:595 (1971).
47. Avdyukova, N.V., E.N. Shmidt, and V.A. Pentegova, Ibid. 6:839 (1971).
48. Morozkov, V.K., E.N. Shmidt, and V.A. Pentegova, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk 128 (1972).
49. Caputo, R., L. Mangoni, P. Monaco, and L. Previtera, Gazz. Chim. Ital. 104:1269 (1974).
50. Avdyukova, N.V., V.A. Raldugin, E.N. Shmidt, and V.A. Pentegova, Khim. Prir. Soedin. 5:653 (1972).
51. Tanka, O., S. Mihvashi, I. Yanagisawa, T. Nikaido, and S. Shibata, Tetrahedron 28:4523 (1972).
52. Avdyukova, N.V., E.N. Shmidt, and V.A. Pentegova, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk 117, 140 (1973).
53. Caputo, R., L. Mangoni, L. Previtera, and R. Iaccarino, Tetrahedron 29:2047 (1973).
54. Caputo, R., L. Previtera, P. Monaco, and L. Mangoni, Ibid. 30:963 (1974).
55. Erdtman, H., B. Kimland, T. Norin, and P.J.L. Daniels, Acta Chem. Scand. 22:938 (1968).
56. Rowe, J.W., and J.H. Scroggins, J. Org. Chem. 29:1554 (1964).
57. Mangoni, L., and R. Caputo, Gazz. Chim. Ital. 97:908 (1967).
58. Lisina, A.I., N.K. Kashtanova, A.K. Dzizenko, and V.A. Pentegova, Izv. Sib. Otd. Nauk SSSR, Ser. Khim. Nauk 165 (1967).
59. Kashtanova, N.K., V.A. Raldugin, and V.A. Pentegova, Aktual. Probl. Izuch. Efirnomaslich. Rast. Efir. Masel 157 (1970).
60. Zinkel, D.F., Tappi 58:118 (1975).
61. Manning, T.D.R., Aust. J. Chem. 26:2735 (1973).
62. Cambie, R.C., P.K. Grant, C. Huntrakul, and R.J. Weston, Aust. J. Chem. 22:1691 (1969).
63. Mamontova, G.A., A.I. Lisina, and V.A. Pentegova, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk 121 (1970).
64. Shmidt, E.N., and V.A. Pentegova, Ibid. 84 (1966).
65. Thomas, B.R., Acta Chem. Scand. 20:1074 (1966).
66. Cheng, Y.S., and E. von Rudloff, Tetrahedron Lett. 1131 (1970).
67. Cheng, Y.S., and E. von Rudloff, Phytochemistry 9:2517 (1970).
68. Hanson, J.R., in "Progress in Phytochemistry," Edited by L. Reinhold and Y. Liwschitz, Vol. 3, Interscience, New York, N.Y., 1972, p. 231.
69. Ribo, J.M., M.R. Mitja, and J. Ramentol, Phytochemistry 13:1614 (1974).
70. Goad, L.J., and T.W. Goodwin, in "Progress in Phytochemistry," Edited by L. Reinhold and Y. Liwschitz, Vol. 3, Interscience, New York, N.Y., 1972, p. 113.
71. Laseter, J.L., R. Evans, C.H. Walkinshaw, and J.D. Weete, Phytochemistry 12:2255 (1973).
72. Bates, R.B., A.D. Brewer, B.R. Knights, and J.W. Rowe, Tetrahedron Lett. 6163 (1968).
73. Nagasampagi, B.A., J.W. Rowe, R. Simpson, and L.J. Goad, Phytochemistry 10:1101 (1971).
74. Osske, G., and K. Schreiber, Tetrahedron 21:1559 (1965).
75. Rowe, J.W., Phytochemistry 4:1 (1965).
76. Rowe, J.W., Tetrahedron Lett. 2347 (1964).
77. Rogers, I.H., and L.R. Rozon, Can. J. Chem. 48:1021 (1970).
78. Rowe, J.W., and E.R. Wagner, 140th National ACS Meeting, September, 1961, p. 83Q.
79. Zinkel, D.F., and F.F. Evans, Phytochemistry 11:3387 (1972).
80. Hemming, F.W., Biochem. J. 113:23P (1969).
81. Feeney, J., and F.W. Hemming, Anal. Biochem. 20:1 (1967).
82. Hemming, F.W., in "Terpenoids in Plants," Edited by J.B. Pridham, Academic Press, New York, N.Y., 1967, p. 223.
83. Wellburn, A.R., and F.W. Hemming, Phytochemistry 5:969 (1966).
84. Lindgren, B.O., Acta Chem. Scand. 19:1317 (1965).
85. Norin, T., and B. Winell, Phytochemistry 13:1290 (1974).
86. Hannus, K., and G. Pensar, Ibid. 13:2563 (1974).

[Received January 17, 1975]