

ANALYSIS AND COMPARISON OF TWO VICTORIAN BROWN COAL RESINITE SAMPLES¹

Ken B. Anderson*, R.E. Botto, G.R. Dyrkacz, R. Hayatsu, and R.E. Winans

Chemistry Division, Argonne National Laboratory,
9700 South Cass Avenue, Argonne, IL 60439

*Also, Department of Organic Chemistry, University of Melbourne,
Parkville, Victoria, Australia 3052

INTRODUCTION

Amongst the organic constituents of coal, the maceral resinite is probably the least complex structurally, due to the relatively simple composition of the original resins. Hence, with careful analysis, it may be possible to construct meaningful and accurate structural descriptions of this maceral. This is especially true of resinites found in low rank coals, where macroscopic resinite accumulations are relatively common, and in which the effects of catagenetic processes are minimal or absent.

For the purposes of this study, two physically diverse resinite samples were obtained from Victorian Brown Coal (VBC) by hand picking from open cut mine faces. The first sample, which is referred to as "resinite" throughout this text is a hard, brittle, glassy material, yellow/brown in colour. The second is a soft, brittle, bone white material, which was found in association with a large gymnosperm log, of undetermined paleobotanical affinity, as sheets between "wood" and "bark". This material is sometimes referred to as "bombicite" by geologists, and is referred to by this name in this text in the interests of clarity. Petrographically, both samples are classified as resinite.

EXPERIMENTAL

Pyrolysis-high resolution mass spectra were recorded on a Kratos MS-50 mass spectrometer, operating at a dynamic resolution of 10 000. Ramped pyrolyses (150-800°C, 50°C/min) were used for pyrolysis of these resins in order to minimize thermal reactions in volatile products. Pyrolysates were introduced into the ion source through an all glass heated inlet system, held at 300°C.²

FTIR spectra were recorded on a Bruker 113V FTIR spectrometer. Samples were quantitatively prepared as 13 mm KBr discs, and spectra normalized to 1.00 mg (resin) for presentation.

CP/MAS ¹³C NMR spectra were recorded on a Bruker CPX-100 NMR spectrometer, operating at a field strength of 2.35 T. Relevant operating parameters were as follows: spectral width = 10 kHz, contact time = 2 ms, pulse repetition rate = 2 sec, proton decoupling field = 56 kHz. Interrupted decoupling experiments used a 100 μs interruption to proton decoupling prior to acquisition.

RESULTS AND DISCUSSION

The results of pyrolysis-high resolution mass spectrometric analysis (Py-HRMS) of the resinite and bombicite samples characterized during the course of this study are illustrated in Figure 1. The close similarity of these data suggests that despite their physical dissimilarity, the chemical structures of these materials are very similar. In particular, these data indicate that species of molecular weight = 302, molecular formula = C₂₀H₃₀O₂ are a predominant subunit in both materials. This suggests that the macromolecular structures of these materials are based predominantly on diterpenoid monomers.

The results of spectroscopic analyses of resinite and bombicite are illustrated in Figures 2 (CP/MAS ¹³C NMR) and 3 (FTIR). The combination of normal CP/MAS ¹³C NMR, CP/MAS ¹³C NMR with interrupted proton decoupling (which reduces or eliminates signal due to protonated carbon) and FTIR, allows considerable

structural detail to be elucidated. Both ^{13}C NMR and FTIR data suggest that both the resinite and bombicite have predominantly aliphatic structures (which is consistent with the elemental composition of these samples - see Table 1). Also indicated is the presence of considerable amounts of oxygen containing functional groups, especially carboxylic acids. The absence of appreciable intensity in the 30 ppm region of the ^{13}C NMR spectra of these samples, and the lack of characteristic dominant IR absorption bands at 2926 cm^{-1} and 2853 cm^{-1} in the corresponding FTIR spectra, rule out the presence of polymethylene structures of significant chain length. Rather, the spectroscopic data suggest that their structures are based to a large extent on alicyclic structures. Strong IR absorbances at 1450 cm^{-1} and 1385 cm^{-1} in the FTIR spectra of both samples suggest a high degree of methyl substitution. Moreover, the partial disappearance of carbon resonances, at 15 ppm, 20 ppm, and 29 ppm in the proton decoupling interrupted ^{13}C NMR spectra, suggests that methyl groups exist in these samples in at least three structurally distinct environments.

^{13}C NMR resonances at 108 and 149 ppm, and moderately intense IR absorption at 887 cm^{-1} indicate the presence of exocyclic $\text{R}_2\text{C}=\text{CH}_2$ structures. Similarly, ^{13}C NMR resonances at 126 ppm and 139 ppm, which are absent and present respectively in the interrupted decoupling spectra, indicate that significant amounts of 1,1,2-trisubstituted $\text{C}=\text{C}$ bonds are present in both samples. Significant carboxyl functionality in these materials is established by ^{13}C resonances at 180-190 ppm and strong FTIR absorbance at 1695 cm^{-1} .

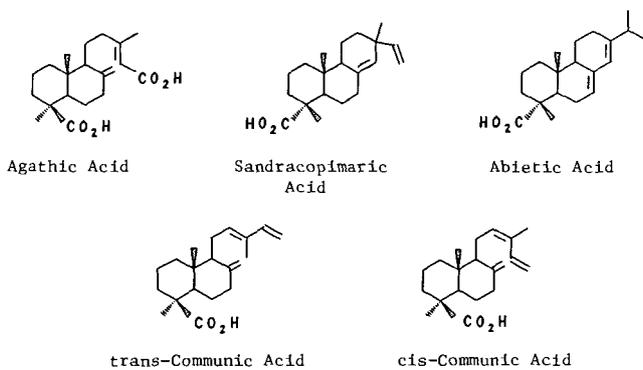
Other types of oxygen containing structures are also indicated by the spectroscopic data, although these differ between samples. The ^{13}C NMR resonance observed at 203 ppm (absent in the interrupted decoupling spectra) and IR absorbance at 1720 cm^{-1} in the spectra of the resinite sample, indicate that aldehydic compounds may contribute significantly to the structure of this material, and ^{13}C resonance at 72 ppm in the spectra of the bombicite sample indicates the incorporation of alcoholic or etheric structures into this material.

The results of analysis therefore suggest that these materials are based on cyclic diterpenoid units, which incorporate a significant degree of methyl substitution. The presence of an exocyclic $\text{C}=\text{C}$ bond, and another, 1,1,2-trisubstituted, $\text{C}=\text{C}$ bond is also indicated, as is the presence of carboxyl functionality. The inclusion of compounds of other structural composition, especially with respect to the nature of oxygen containing functional groups, is also indicated, but the structural units having the features described above appear to predominate, and are common to both samples.

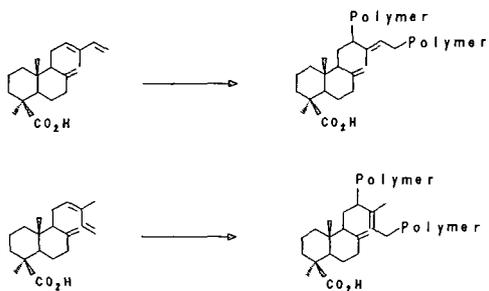
It has been noted that macroscopic resinite accumulations in VBC often occur in association with fossil logs of the genus *Agathis*. This association has not been specifically established for the samples used in this study, except, as already noted, that the bombicite sample characterized was found in intimate association with a large gymnosperm log. Nevertheless, this relationship has been established for a significant number of closely similar samples, and it is highly probable that the samples used in this study are derived from the bled resins of this species.

Modern *Agathis* resins were at one time of considerable commercial value, and as such, have been the subject of numerous investigations. Analysis of fresh bled resins of this species have demonstrated that the major components present are diterpenoid acids, specifically, those with the structures illustrated in Scheme 1. It has also been established that the solvent extracts of VBC resinites are rich in these acids, especially agathic acid, and their degradation products.³⁴

Based largely on the foregoing work, and more recently on spectroscopic evidence, previous workers have proposed structures for these resinites based on poly-agathic acid.³⁵ The mechanism proposed by these workers suggests that these resinites are formed by polymerization of (mainly) agathic acid with loss of the terminal $\text{C}-15$ carboxyl group. Such a polymeric structure would therefore be based predominantly on C_{10} monomers. The results of the analyses reported here however, clearly demonstrate the predominance of C_{20} products in both VBC resinite and bombicite, and hence preclude C_{10} monomers as a major structural subunit in these samples. The structure proposed by these authors,³⁵ however, very closely resembles those which can be drawn for the polymerization products of cis- and trans-communic acids, (as illustrated in Scheme 2), which are major components of fresh *Agathis* resins.⁶ These acids are known to readily polymerize on exposure to the atmosphere, and in some cases, poly-Communic acids have been shown to constitute a significant fraction of fresh and recent resins.⁷



Scheme 1.



Scheme 2.

CONCLUSIONS

The results of this study of VBC resinites suggest that these materials are not based on poly-agathic acid structures as has been previously proposed. The data obtained indicate the predominance of structural subunits of molecular formula $C_{20}H_{30}O_2$, which are consistent with a poly-communic acid based polymeric resinite structure. Other materials may be incorporated into the polymeric structure to a lesser degree, and may also be physically occluded within it.

ACKNOWLEDGMENTS

This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under contract number W-31-109-ENG-38. The authors would like to thank Dr. T. V. Verheyen, Coal Corp. of Victoria, for supplying the samples used in this study.

REFERENCES

1. Based in part on: Anderson, K.B. (1989), PhD Thesis, University of Melbourne.
2. Winans, R.E., McBeth, R.L. and Neill, P.H. (1988), ACS Division of Fuel Chem. Preprints, 33(3): 85-90.
3. Brooks, J.D. and Steven J.R. (1967), Fuel, 46: 13-18.
4. Allan, J. (1975), PhD Thesis, University of Newcastle-upon-Tyne.
5. Wilson, M.A., Collin, P.J., Vassallo, A.M. and Russell, N.J. (1986), Org. Geochem. 7(2): 161-168.
6. Thomas, B.R. (1969), In: "Organic geochemistry - methods and results", G. Eglinton and M.T.J. Murphy (eds), Springer-Verlag, N.Y. pp 599-618.
7. Carman, R.M., Cowley, D.E. and Marty, R.A. (1970), Aust. J. Chem., 23: 1655-1665.

TABLE 1.

	Elemental Composition (wt%)					Molecular Formula (based on C_{20})
	C	H	N	S	O	
Resinite	79.78	10.19	-	0.03	10.00	$C_{20}H_{30.6}O_{1.8}$
Bombicite	75.17	9.47	-	0.06	15.31	$C_{20}H_{30.2}O_{3.1}$
poly-Communic Acid	79.5	9.9	-	-	10.6	$C_{20}H_{30}O_2$

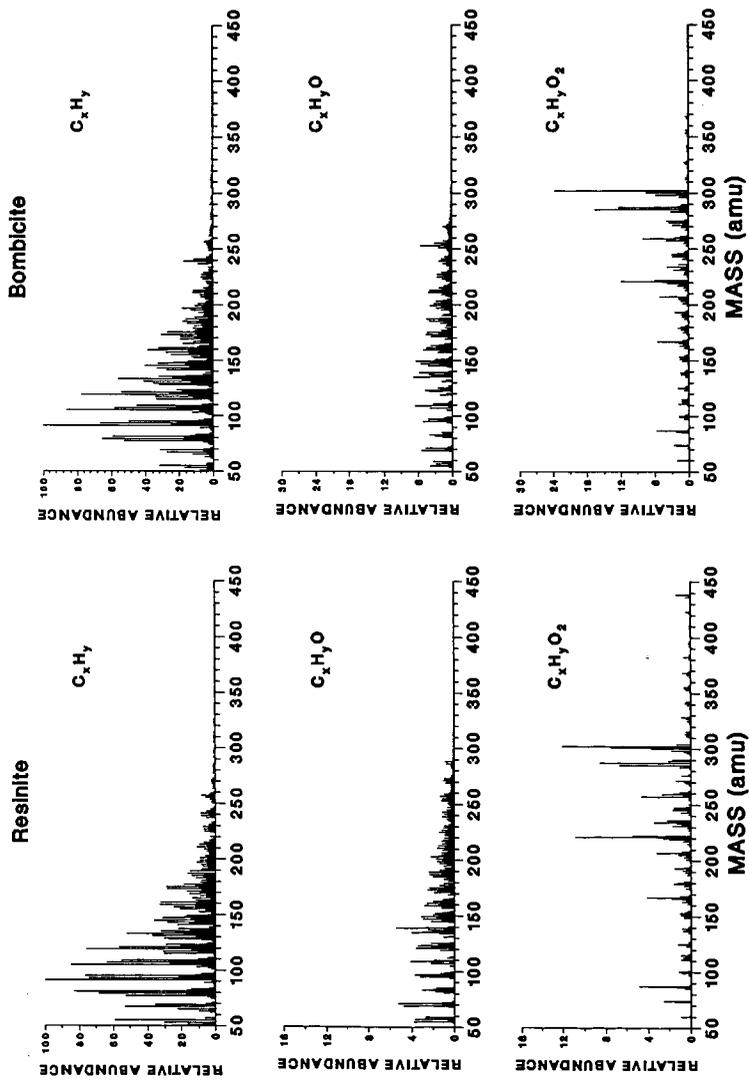


Figure 1. Mass spectra of selected ion classes obtained by Py-HRMS of VBC resinite and bombicite (averaged over 50 scans).

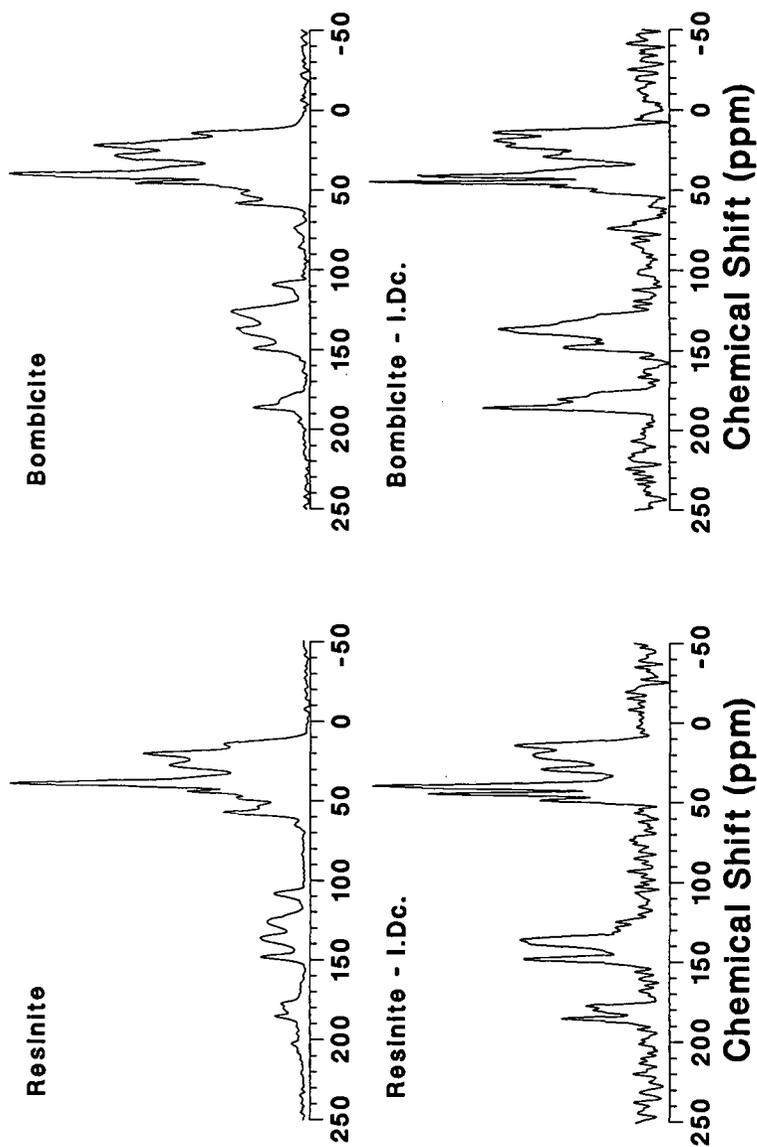


Figure 2. CP/MAS ^{13}C NMR spectra, and Interrupted Proton Decoupling (I.Dc.) CP/MAS ^{13}C NMR spectra of VBC resinite and bombicite.

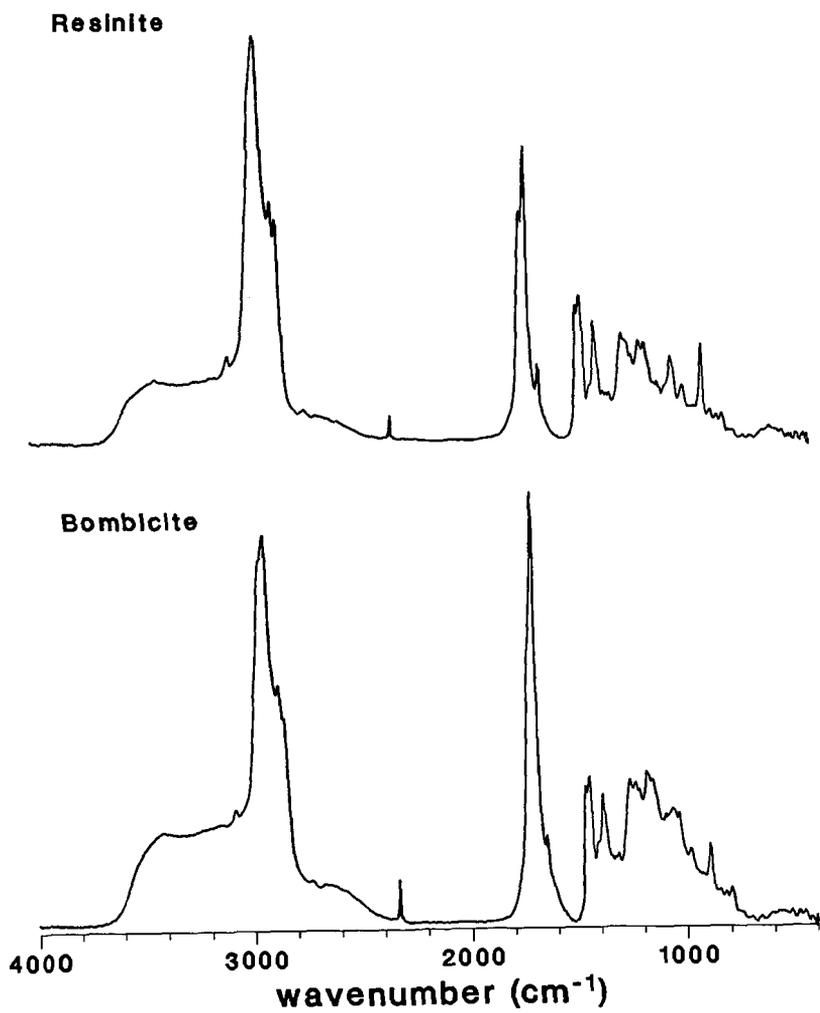


Figure 3. FTIR spectra of VBC resinite and bombicite.