Amber from Japan: a Nuclear Magnetic Resonance Study[1]

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Abstract: Fifteen amber samples from Japan have been analyzed by nuclear magnetic resonance spectroscopy. The nine distinct geographical sources extend from the northern island of Hokkaido to the southern tip of the main island of Honshū. All but one sample gave the characteristic patterns of Group A amber. One of these, from Shiga Prefecture, gave variations of this spectral pattern suggesting a considerably younger or less fully matured condition within Group A. The fifteenth sample, from Mizunami in Gifu Prefecture, gave the clear pattern of Group B amber, which differs significantly from Group A in having an angiospermous (flowering) rather than a coniferous plant source.

Introduction

   Amber has been culturally important in Japan since antiquity. Wider appreciation of Japan as a major source of amber dates particularly from about 2006, when the Kaliningrad Amber Museum put on a major exhibit of Japanese amber (Sasaki 2006). Schlee (1990) and Aizawa (2002) have summarized the many Japanese sources of amber, which extend from the northern island of Hokkaido to the southern island of Kyushu, although most sources are on the eastern side of the main island of Honshū (Figure 1). The most productive region is from the vicinity of the town of Kuji at the northern end of Honshū in the Prefecture of Iwate (point 2 on Figure 1). Amber from Kuji tends to come from the Santonian and Campanian stages of the Late or Upper Cretaceous, about 72-86 million years ago (mya), although older samples extend into the Aptian (>100 mya, Early/Upper Cretaceous) and the Oligocene (ca. 30 mya, Tertiary/Paleogene). Schlee (1990) described the richness of these sources from estimates that the 20 Kuji mines produced about 350 tons of amber per year (in about 1938). Kimura et al. (2005) characterized the amber pieces as being lenticular (lens shaped) in the Kuji group and teardrop shaped in the Noda group (Noda is a village in Iwate close to Kuji). Mining sources in other parts of Japan

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have younger beds, including Miocene (7-23 mya), Pliocene (2.6-5.3 mya), and even Pleistocene (< 2.6 mya).

Figure 1. Amber sources examined in this study, listed by town and prefecture. (1) Mikasa, Hokkaido. (2) Kuji, Iwate. (3) Iizaka-machi, Fukushima. (4) Iwaki, Fukushima. (5) Chōshi, Chiba. (6) Mizunami, Gifu. (7) Kobe (Kizu, Oshibedani-machi), Hyōgo. (8) Konan (Kōsei-chō), Shiga. (9) Ube, Yamaguchi.

The techniques described by Schlee (1990) for examination of amber are of traditional types: color (opaque yellow/orange/red/brown, rarely colorless or blue), solubility in alcohol, appearance under ultraviolet light, and presence of sparks on burning.   To our knowledge, no comprehensive spectroscopic investigation of Japanese amber has been carried out in order to learn about its molecular structure. Consequently, we have assembled a collection of Japanese amber from representative locations and have examined them by nuclear magnetic resonance (NMR) spectroscopy.

Curt Beck (1986) pioneered the use of infrared spectroscopy for the characterization of amber. This method was successful in identifying amber primarily from the Baltic Sea, which we have termed Group C in the NMR context, but Beck's approach was not useful for amber with other provenances. NMR examination of solid amber (Lambert and Frye 1982) succeeded in providing a method that could differentiate at least five groupings of amber. Mass spectrometry provided a parallel method (Anderson et al. 1992, Lambert et al. 2008).   The primary advantage of the original NMR method is that it examines bulk material, reporting on the environments of carbon nuclei (specifically, the magnetically active, stable ^{13}C isotope), which form the skeleton of the amber structure. It does not identify specific molecules but provides distinctions via different spectral patterns. Mass spectrometry has a considerable advantage in its sensitivity and hence the smaller amount of material required for analysis, and it identifies specific small molecules from the macromolecular structure. The volatilization process, however, is selective, so that analysis does not necessarily reflect the entire bulk. Solution phase NMR studies of hydrogen atoms (protons or the ^{1}H isotope) in amber offer higher sensitivity than the bulk studies with ^{13}C , but incomplete solubility means that the spectra are not necessarily representative of the bulk (Lambert et al. 2012). We use a combination of carbon NMR analysis of the bulk and proton NMR analysis of solutions to provide comprehensive characterization of amber. A two-dimensional ^{1}H spectrum constitutes the only published spectroscopic report on Japanese amber to our knowledge (Lambert et al. 2012). Herein we report the carbon and proton NMR spectral results on fifteen samples from nine distinct sources in Japan.

Methods

Table 1 contains descriptions of the 15 Japanese samples plus comparison samples and provides their sources. Detailed description of the methods has been published previously (Lambert et al. 2012, 2013).

Table 1. Sources of Japanese ambers and related materials.

Sample Number	Country	Location (on Figure 1)	Provider
1545	Japan	(1) Ponbetsu-gawa, Mikasa, Hokkaido Prefecture	Teruhisa Ueno, Fukuoka, Japan
828	Japan	(2) Okawame, Minami-ku-noke, Rikuchū, Iwate Prefecture	C. D. Brown, National Museum of Natural History, Dept. of Mineral Sciences, Washington, DC, USA, sample 47140
829	Japan	(2) Kudo-Gori, Rikuchū, Iwate Prefecture	C. D. Brown, National Museum of Natural History, Dept. of Mineral Sciences, Washington, DC, USA, sample 11877
899	Japan	(2) Kuji, Iwate Prefecture	P. R. Craig, Kuji Amber Museum, Kuji, Japan
1543	Japan	(2) Kuji, Iwate Prefecture	Teruhisa Ueno, Fukuoka, Japan
1232	Japan	(2) Wano, Kuji, Iwate Prefecture	K. Uemura, National Science Museum, Ueno Park, Taito-ku, Tokyo, Japan
830	Japan	(3) Iizaka-machi, Fukushima Prefecture	C. D. Brown, National Museum of Natural History, Dept. of Mineral Sciences, Washington, DC, USA, sample 140825
1231	Japan	(4) Ohisa, Iwaki, Fukushima Prefecture	T. Suzuki, gift of K. Uemura, National Science Museum, Ueno Park, Taito-ku, Tokyo, Japan
1542	Japan	(4) Ohisagawa (Ohisa River), Ohisa-machi, Iwaki, Fukushima Prefecture	Teruhisa Ueno, Fukuoka, Japan
1544	Japan	(5) Nagasaki-Tokawa, Chōshi, Chiba Prefecture	Teruhisa Ueno, Fukuoka, Japan

1643	Japan	(6) Kamado, Mizunami, Gifu Prefecture	Teruhisa Ueno, Fukuoka, Japan
1641	Japan	(7) Kizu, Oshibedani-machi, Kobe, Hyōgo Prefecture	Teruhisa Ueno, Fukuoka, Japan
1642	Japan	(7) Kizu, Oshibedani-machi, Kobe, Hyōgo Prefecture	Teruhisa Ueno, Fukuoka, Japan
1646	Japan	(8) Yasugawa (Yasu River), Konan, Shiga Prefecture	Teruhisa Ueno, Fukuoka, Japan
1645	Japan	(9) Fujiyama, Ube, Yamaguchi Prefecture	Teruhisa Ueno, Fukuoka, Japan
1640	United States	Harrell Station near Selma, University of Alabama field station, Dallas Co., Alabama	T. Lynn Harrell Jr., gift of Dana J. Ehret, Curator of Paleontology, University of Alabama Museums, Tuscaloosa, Alabama, USA
1664	Russia	Yantardakh Hill, Maimetsha River, a branch of the Kheta River, Khatanga Basin, East Taimyr Peninsula, North Siberia	Expedition of the Paleontological Institute of the USSR Academy of Sciences, gift of the Dept. of Paleobiology, National Museum of Natural History, Smithsonian Institution, Washington, DC, USA

Amber from Iwate Prefecture (Kuji), Honshū

Our study group includes five samples from Iwate Prefecture at the northern extreme of Honshū Island. Three (899, 1232, 1543) were labeled simply as Kuji city, although one of these (1232) was further labeled as Wano, a term that may refer to the Wano Formation or to the town of Wano near Kuji. A fourth sample (828) was labeled Okawame, Minami-ku-noke, Rikuchū. The town of

Okawame became part of Kuji city in 1954. It was located in the old province of Rikuchū, which became part of Iwate Prefecture. Thus the samples labeled Rikuchū are classified with those from Kuji. The fifth sample (829) was labeled Kudo-Gori, Rikuchū. Colors varied from yellowish orange to dark orange to red to nearly black. The samples also varied from translucent to opaque to banded. Schlee (1990) called samples with the last characteristic as being "agate-banded pieces: akin to the Lebanon amber, the banding consists of interchanging layers of clear amber." Alternatively, such an appearance may be described as marbleized. The five Iwate samples came from four different donors.

   Figure 2 illustrates two modes of recording the ^{13}C spectrum of sample 899. Throughout this paper, the lower portion represents a basically complete spectrum, in which all the carbon atoms have been decoupled from interactions with neighboring hydrogen atoms, in order to clarify the spectrum and to provide enhanced sensitivity (Lambert and Mazzola 2004). The upper spectrum has focused the decoupling process, so that resonances from most carbons with directly attached hydrogen atoms disappear. The process is called dipolar dephasing or interrupted decoupling and provides an alternative pattern analysis for distinguishing classes of amber. The symbol δ is used to represent the unit of frequency, which historically is expressed as parts per million of the magnetic field.
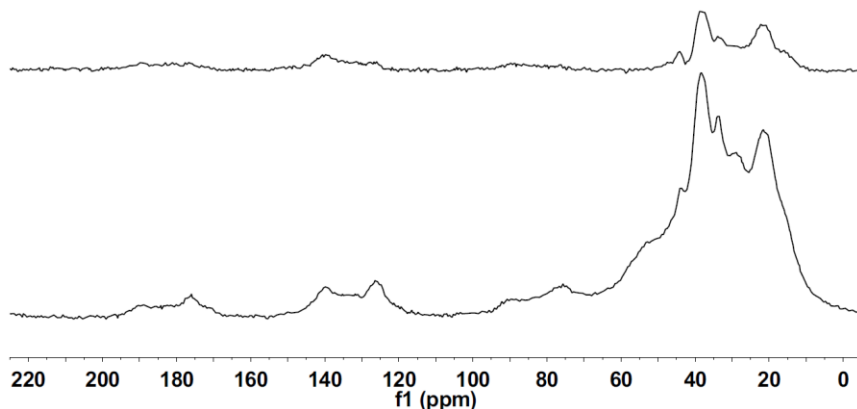

Figure 2. The solid state ^{13}C spectrum of sample 899 from Kuji, Iwate Prefecture, with normal decoupling (lower) and with dipolar dephasing (upper). The broad peaks at δ 70-90 and 170-190 are artifacts of the spinning process: spinning sidebands of the unsaturated peaks at δ 120-140.

   The normal spectrum is dominated by saturated carbon atoms (δ 10-60). In addition, there are weak peaks in the region δ 120-145, which come from unsaturated (alkenic) carbon atoms. More specifically, they are from carbon atoms that are in a ring or chain and bear one or no hydrogen atom (>C==CH), rather than terminal functionalities known as exomethylene groups, >C==CH$_2$, which resonate at δ ca. 110 (==CH$_2$) and 150 (>C==). The congruent peaks at δ

70-90 and 170-190 are spinning sidebands, which are artifacts of the spinning process.

These spectra constitute the classic pattern of Group A amber (mass spectral Class Ib) (Lambert et al 2008). Each amber group exhibits a common NMR (and mass spectral) signature, implying a common botanical origin. Group A is the largest and most widespread amber grouping, with samples found in North America, Greenland, Europe (Western, Central, and Eastern), Southwest Asia (the Middle East), South Asia (India), North Siberia, East Asia (China, Japan), Australia, and New Zealand. Group A samples from the Pacific (Lambert et al. 1993) have been related spectroscopically with the Araucariaceae, a coniferous family, and samples from Southeast and Southwest Asia (Poinar and Milki 2001) have been related to the same family through identification of plant parts. Other Group A ambers, as well as the closely related Group C (Baltic) ambers, also have coniferous sources, for which various families have been suggested (Langenheim 2003). For comparison, Figure 3 presents the spectra of sample 1640 from Selma, Dallas Co., Alabama, typical for European and North American samples. There are strong similarities but a few differences between the spectra of Figures 2 and 3. Both spectra with normal decoupling are dominated by resonances of saturated carbons with the strongest peak at δ ca. 40, and both spectra have weak alkenic peaks at δ 120-145 (plus spinning sidebands). One difference in fine structure is the peak at δ 36 in Figure 2, a characteristic of East Asian Group A samples. The samples have very similar and characteristic spectra with interrupted decoupling (three main peaks plus shoulders). Samples from North Siberia (East Taimyr Peninsula) have very similar spectra, including the peak at δ 36 with normal decoupling (Figure 4).
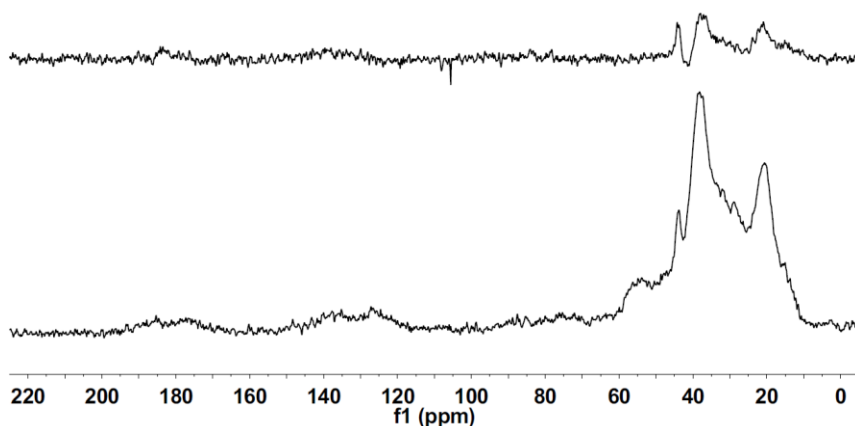

Figure 3. The solid state ^{13}C spectrum of sample 1640 from Harrell Station near Selma, Dallas Co., Alabama, with normal decoupling (lower) and with dipolar dephasing (upper).
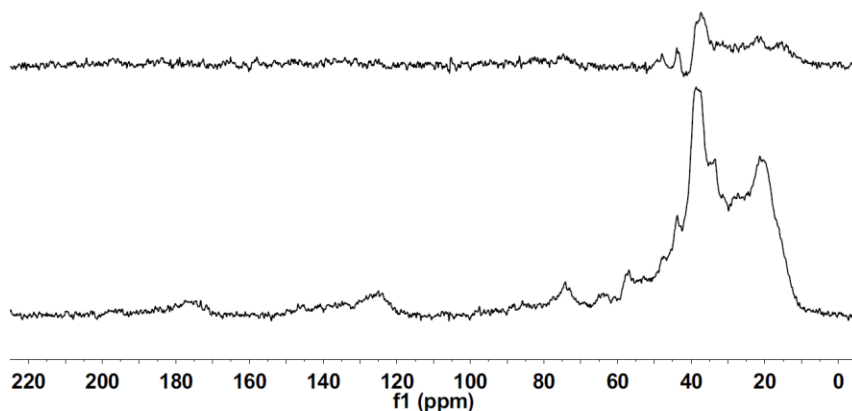
Figure 4. The solid state [13C] spectrum of sample 164 from Yantardakh Hill, Maimetsha River, a branch of the Kheta River, Khatanga Basin, East Taimyr Peninsula, North Siberia, Russia,with normal decoupling (lower) and with dipolar dephasing (upper).

Proton magnetic resonance also provides distinctions between amber groups. Figure 5 presents the one-dimensional spectrum of the protons of sample 899 from Kuji. It is dominated by peaks in the saturated region. The peak at δ 0 is from the standard, tetramethylsilane [$(CH_3)_4Si$], and the peak at δ 7.3 is from residual, undeuterated solvent, $CHCl_3$. The pattern is characteristic of samples from Group A, for which generally three saturated groupings occur, centered at δ ca. 0.9. 1.3, and 1.7. In addition, there are weak peaks in the region of hydrogens close to electron-withdrawing groups (δ 2.0-4.0), hydrogens on alkenic carbons (δ ca. 5), and hydrogens on aromatic rings (δ ca. 7).

Figure 5. The 1D ^{1}H spectrum of sample 899 from Kuji, Iwate Prefecture, in chloroform-*d*.

The two-dimensional COSY spectrum is given in Figure 6. This acronym stands for COrrelation SpectroscopY. The spectrum has two identical frequency dimensions, respectively on the *x* and *y* axes, and intensity is a third dimension roughly represented by the size of the observed peaks (the plot is a contour representation of the bases of the actual peaks). So-called cross peaks off the diagonal occur only when two hydrogen atoms interact through a coupling process. The diagonal represents the one-dimension spectrum plus various artifacts, and the cross peaks occur symmetrically on either side of the diagonal (at A/B and B/A, for which A and B are the 1D resonance frequencies of interacting nuclei). The cross peaks at 3.3/3.5 generally are characteristic of Group A ambers.

Figure 6. The 2D COSY spectrum of sample 899 from Kuji, Iwate Prefecture, in chloroform-*d*.

For comparison, Figures 7 and 8 provide the 1D and 2D spectra for sample 1640 from Selma, Alabama. Samples from North America (north of Mexico) usually fall into Group A (Lambert et al. 2012). The 1D spectrum is very similar to that of sample 899 (with the three strong peaks in the saturated region), except that the two peaks close to δ 3.4-3.8 and the alkenic peaks at δ 4.8-5.4 are more intense and the saturated peak at δ 1.7 less intense. The 1D spectrum of the Siberian sample 1664 (Figure 9) also are similar to those of the Kuji samples (as well as the Alabama sample). All three COSY spectra (Figures 6, 8, and 10) have the same pattern in the region δ 3-4, although the comparison is not easy because Figure 10 is much more intense. All three have the characteristic cross peaks at 3.3/3.5, as well as the pair at 3.5/3.7.

Figure 7. The 1D ^{1}H spectrum of sample 1640 from near Selma, Alabama, in chloroform-*d*.
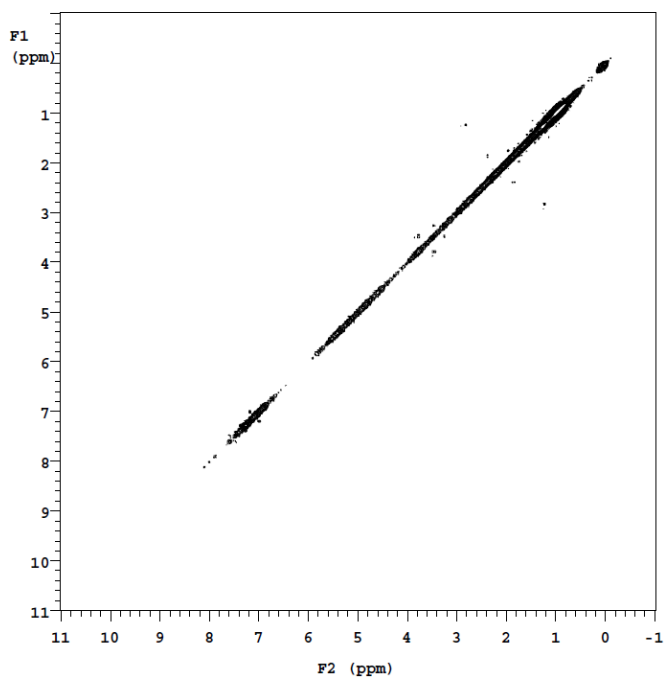

Figure 8. The 2D COSY spectrum of sample 1640 from near Selma, Alabama, in chloroform-*d*.
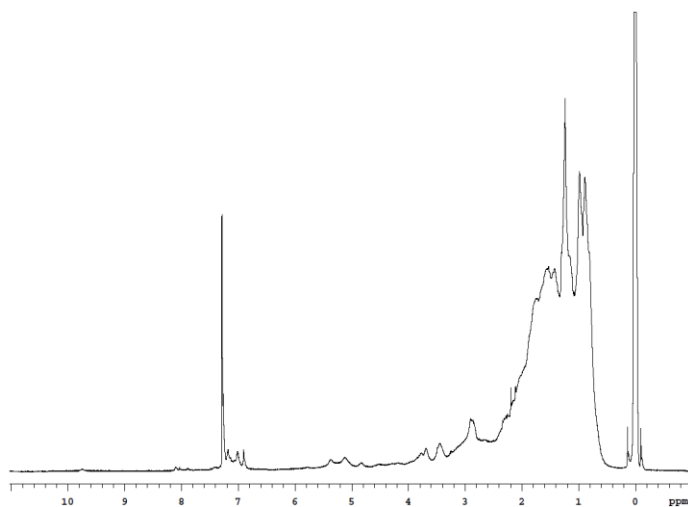
Figure 9.   The 1D ^{1}H spectrum of sample 1664 from the East Taimyr Peninsula, North Siberia, Russia, in chloroform-*d*.
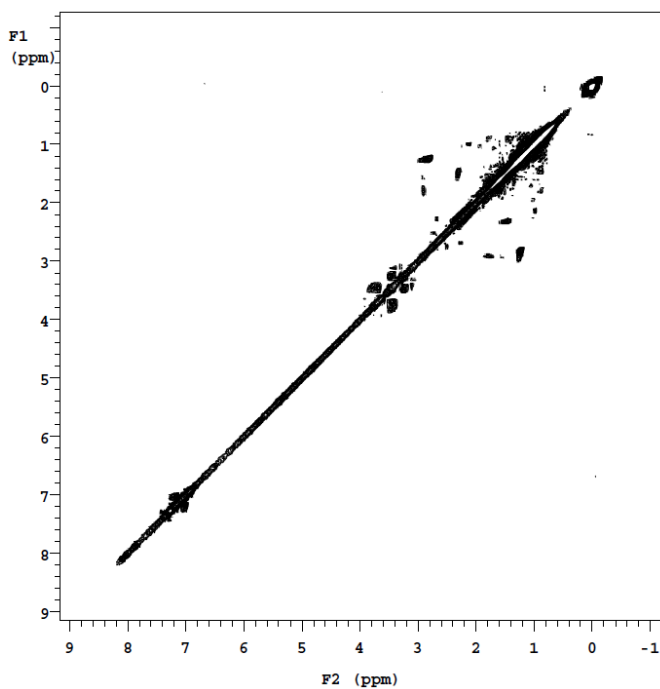

Figure 10.   The 2D COSY spectrum of sample 1664 from the East Taimyr Peninsula, North Siberia, Russia, in chloroform-*d*.

Amber from Hokkaido

   Schlee (1990) noted that small pieces of amber have been found at several sites on the northern island of Hokkaido, including samples with a blue color. He quoted the age of the beds as Upper Eocene (ca. 34-40 mya). Both Schlee (1990, Picture 28) and Aizawa (2002, Figure 4) located four amber sources on Hokkaido in their maps of Japan.   Aizawa primarily described sources associated with the Ishikari coalfield in west central Hokkaido and gave a general date of the Paleogene Period (23-66 mya), which includes the Eocene. Our single sample from Hokkaido came from the Ponbetsu coalfield, part of the greater Ishikari field near Mikasa city, (Figure 1, point 1). Its solid state ^{13}C spectrum (Figure 11) places the Ishikari amber in Group A. It differs in fine structure from the spectra from Kuji (Figure 2) but not in overall character. The sample did not have sufficient solubility to provide useful proton spectra.
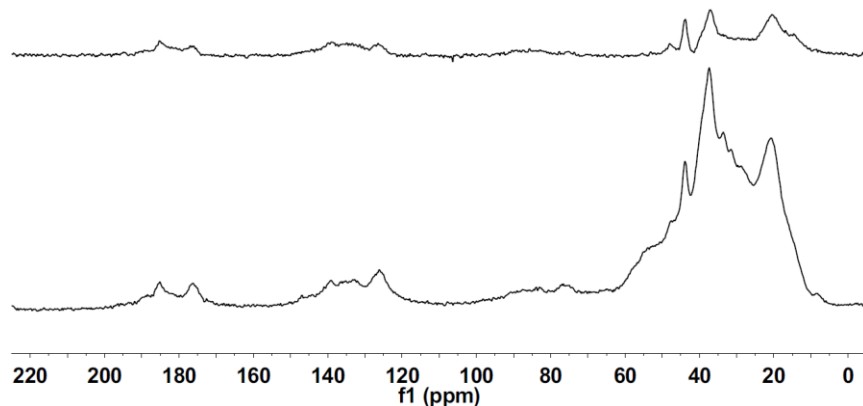

Figure 11.   The solid state ^{13}C spectrum of sample 1545 from Ponbetsu, Mikasa, Hokkaido Prefecture, with normal decoupling (lower) and with dipolar dephasing (upper).

Amber from Additional Sources on Honshū North of Tokyo

   Schlee (1990) mentioned two sites between Tokyo and Kuji that have produced modest amounts of amber. Samples from the city of Iwaki, Fukushima Prefecture, some 200 km north of Tokyo (Figure 1), come primarily from the Santonian stage (84-86 mya) of the Cretaceous period, although some are said to come from the Oligocene, similar to the situation with Kuji amber. The oldest Japanese samples found to date came from Chōshi city, Chiba Prefecture, about 100 km northeast of Tokyo on the Pacific coast. According to Schlee, they date to the Lower Aptian stage (113-125 mya) of the Lower Cretaceous period. Aizawa (2002) also noted amber from Chōshi with an Aptian date. Both sources

mentioned that some of the Chōshi amber constitutes loose stones found on the beach after storms, but other materials were associated with specific geological provenance. Aizawa also mentioned amber from the Joban coal field in the Iwaki city area (specifically Ohisa-machi), associated with Paleogene period (23-66 mya).

We have examined four samples from this general region. Sample 1231 came from Ohisa, Iwaki city, and sample 1542 from Ohisagawa, Ohisa-machi, Iwaki. Sample 1231 was labeled as coming from the Santonian formation of the Late Cretaceous and sample 1542 from the Upper Cretaceous, ca. 85 mya. Sample 830 also came from Fukushima Prefecture, from Iizaka town, close to Iwaki (Figure 1, Points 3 and 4). Our fourth sample (1544) came from Chōshi in Chiba Prefecture.

The ^{13}C spectra of the solids (Figure 12 for sample 1544 from Chōshi) for these four samples closely resemble those illustrated in Figures 2 and 11; the proton spectra of the solutions show some variations, within the normal range of Group A materials. The 1D ^{1}H spectrum of sample 830 from Iizaka contains two of the three normal saturated groupings at δ 0.9. 1.3, and 1.7 and an identical pattern of peaks in the electron-withdrawing region (δ 2.0-3.0), almost entirely lacking, however, the large peak at δ 1.7. The 1D spectra of samples 1542 from Iwaki and 1544 from Chōshi are very similar, with weaker peaks in the electron-withdrawing and aromatic regions and a slightly different pattern in the saturated region (Figure 13). The proton spectra provide greater variability than the carbon spectra but still represent the range of Group A materials and are quite different from spectra of Groups B and D (Group C, Baltic amber, is a variant of Group A, distinguished by the presence of resonances from the diagnostic component, succinic acid).
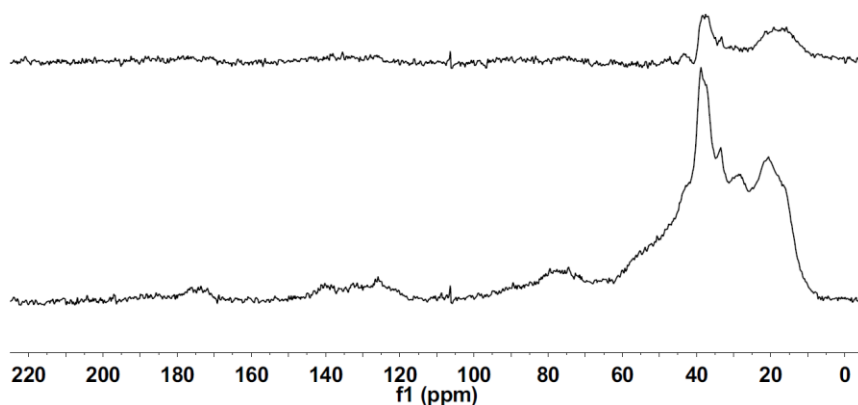

Figure 12. The solid state ^{13}C spectrum of sample 1544 from Chōshi, Chiba Prefecture, with normal decoupling (lower) and with dipolar dephasing (upper).
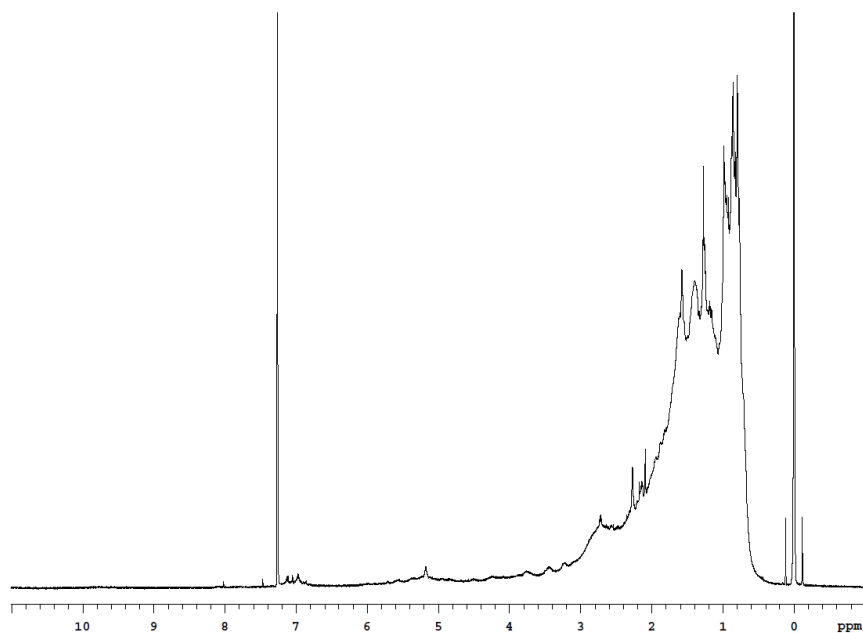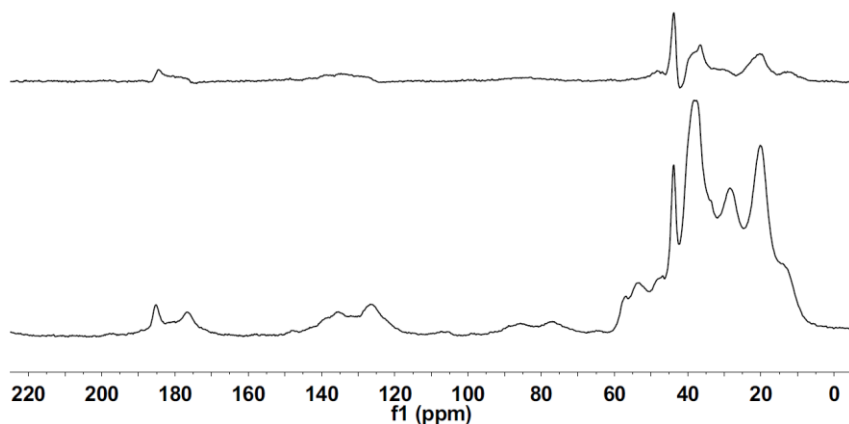
Figure 13.   The 1D ^{1}H spectrum of sample 1544 from Chōshi, Chiba Prefecture, in chloroform-*d*.

Amber from Additional Sources on Honshū South of Tokyo

The city of Hachiōji (part of the Tokyo Metropolitan Prefecture just west of Tokyo) has provided small amounts of amber, estimated to be from the Pliocene (2.5-5 mya) or even more recent periods.   Schlee (1990) suggested that the material may not be fully fossilized. A second source of relatively recent amber is Mizunami, which is treated separately in the next section. The large city of Kobe in the Hyōgo Prefecture portion of the Kansai region of southern Honshū, 425 km southwest of Tokyo, was an important source of amber from the middle Miocene (10-15 mya) (Schlee 1990).   Ube in the southernmost corner of Honshū, 850 km from Tokyo in Yamaguchi Prefecture has been a rich source of amber from the Upper Eocene (ca. 34-40 mya), including rare bluish materials (Schlee 1990). Other minor sources have been found in Okayama, Mie, and Kagawa Prefectures, generally around the Inland Sea separating Honshū from Shikoku (Schlee 1990 and Aizawa 2002).

We have studied five samples from regions on Honshū south of Tokyo, one of which is considered in the next section. The remaining are two samples from Kobe (Figure 1, point 7, 1641 and 1642), one from Ube (point 9, 1645), and one from a source not mentioned by Schlee or Aizawa, the Yasu River in Kōsei-chō

(now part of Konan city), Shiga Prefecture (point 8, 1646). The samples from Kobe and Ube give carbon spectra (Figure 14) very similar to those of Figures 2 and 11. Sample 1646 from Shiga Prefecture is clearly a member of Group A but exhibits clear resonances in the unsaturated region from exomethylene carbons (>C==CH$_2$) at δ ca. 110 (==CH$_2$) and 150 (>C==) (Figure 15). Such resonances are associated with younger or less mature ambers, which have not suffered the diagenetic processes that remove such functionalities, as observed frequently in European (Lambert et al. 1988) and Dominican (Lambert et al. 1985) materials.

Figure 14. The solid state ^{13}C spectrum of sample 1645 from Ube, Yamaguchi Prefecture, with normal decoupling (lower) and with dipolar dephasing (upper).
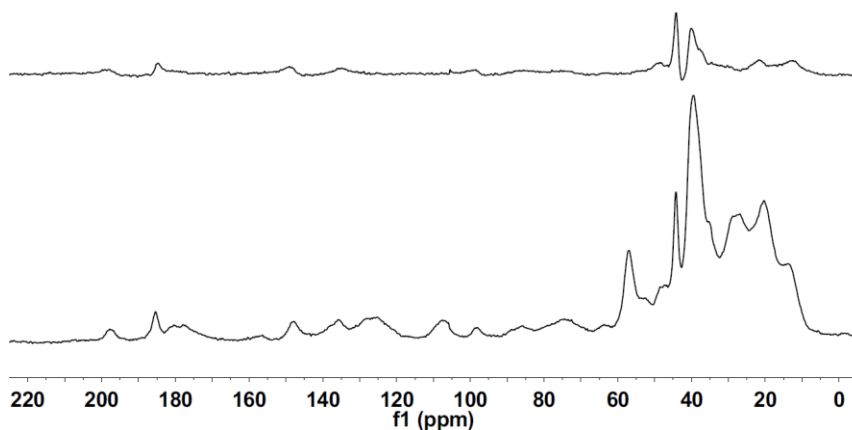

Figure 15. The solid state ^{13}C spectrum of sample 1646 from Kōsei-chō, Shiga Prefecture, with normal decoupling (lower) and with dipolar dephasing (upper).

The ¹H spectra of samples 1641, 1642, and 1645 are normal for Group A ambers (Figure 16), as are the COSY spectra (Figure 17). The proton spectra of sample 1646, however, exhibits appreciable differences. The 1D spectrum (Figure 18) has the basic elements expected for Group A, but both the saturated and unsaturated areas are richer. The COSY spectrum (Figure 19) also is richer, with a stronger cross peak at 3.3/3.5 and a clear cross peak at 4.9/5.8, which occurs in some Group A samples and is strongly characteristic of conifer sources (Lambert et al. 2012). The richer nature of these spectra is characteristic of younger samples and is consistent with similar aspects of the ¹³C spectra of the same sample (Figure 15).

Although our sample set included none from the southern island of Kyushu, both Schlee (1990) and Aizawa (2002) cited several such sources.
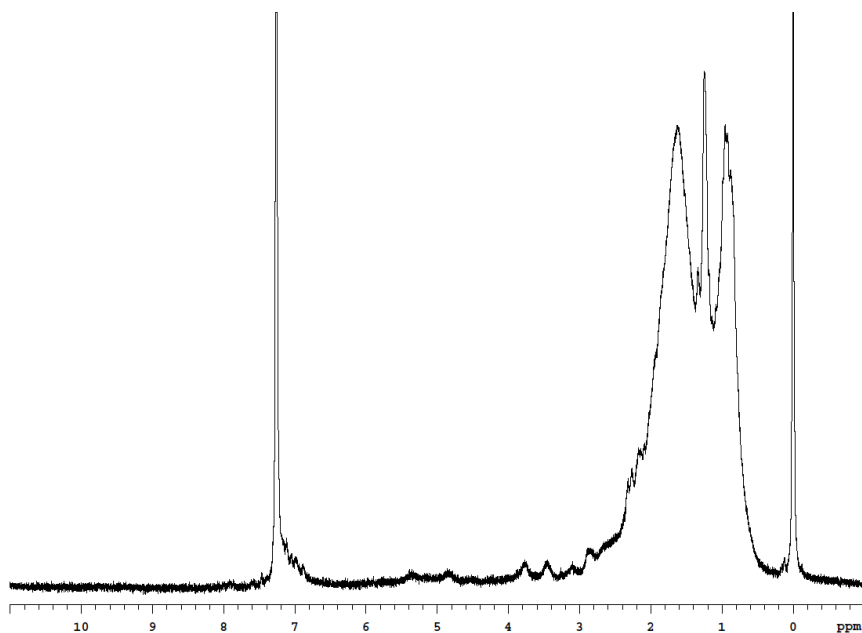

Figure 16. The 1D ¹H spectrum of sample 1641 from Kobe, Hyōgo Prefecture, in chloroform-*d*.
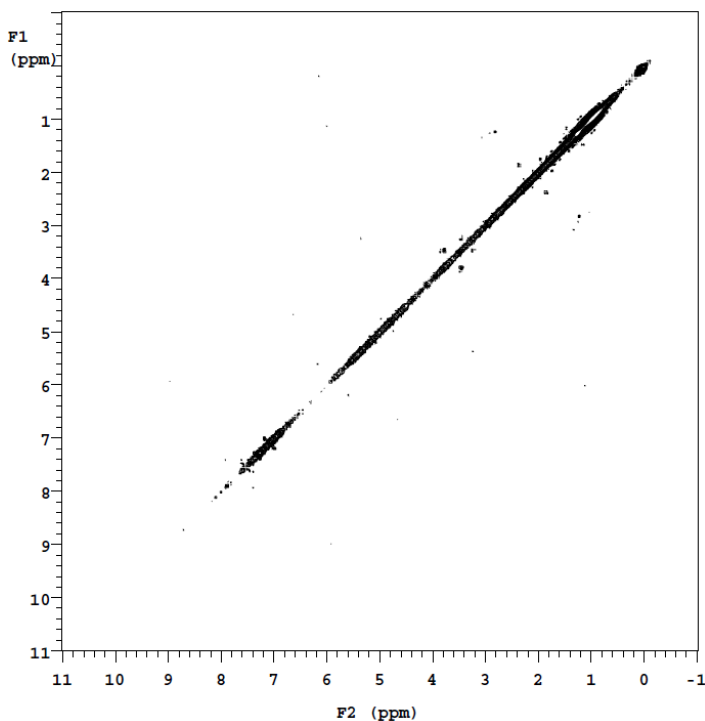
Figure 17. The 2D COSY spectrum of sample 1641 from Kobe, Hyōgo Prefecture, in chloroform-*d*.
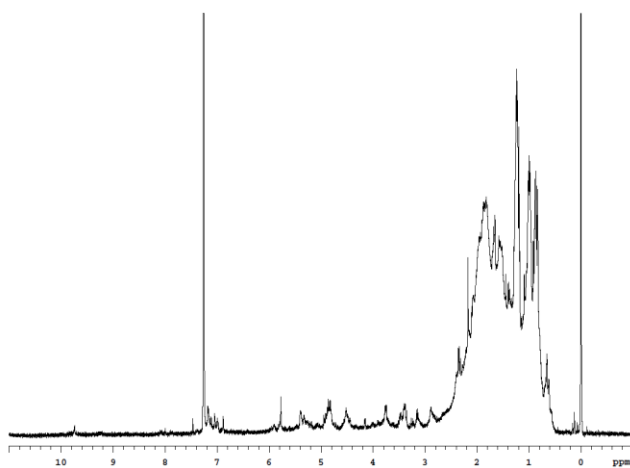

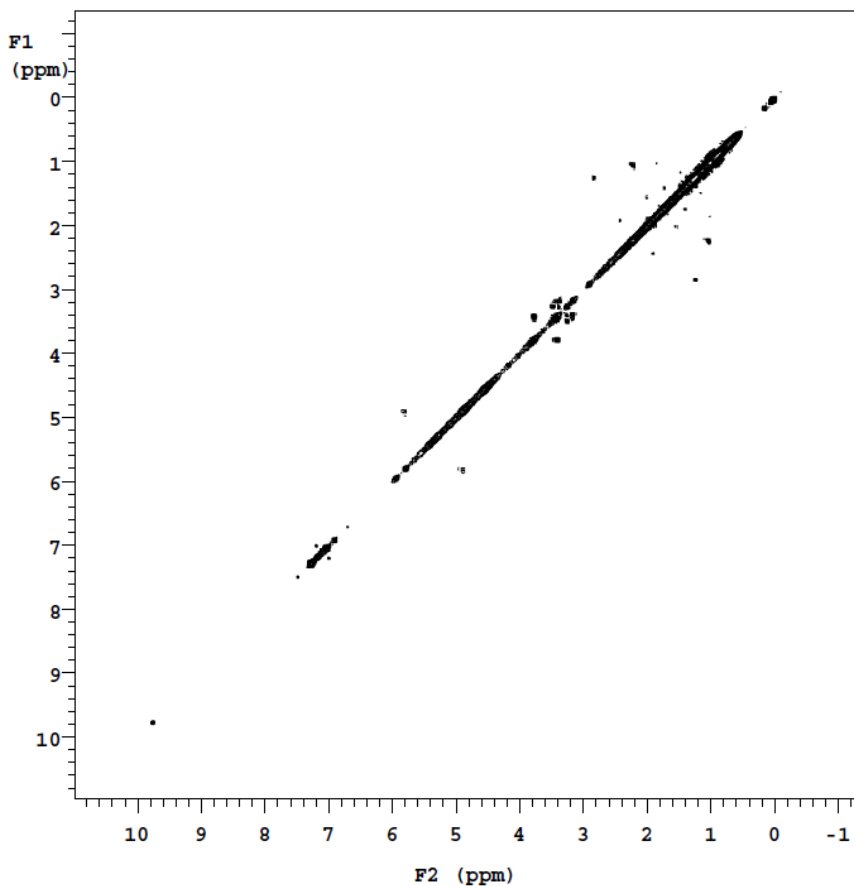Figure 18. The 1D ¹H spectrum of sample 1646 from Kōsei-chō, Shiga Prefecture, in chloroform-*d*.

Figure 19. The 2D COSY spectrum of sample 1646 from Kōsei-chō, Shiga Prefecture, in chloroform-*d*.

Amber from Mizunami City, Gifu Prefecture

All the samples described to this point have been members of Group A. Indeed, all samples we heretofore have examined from East Asia, including China and Siberia, have fallen into this group, which, as generally agreed, derives from conifer sources. Sample 1643 from Mizunami (Figure 1, point 6) therefore came as a considerable surprise, as its spectra were characteristic of Group B, which derives from flowering plants, most likely from the Dipterocarpaceae (Lambert et al. 2013). Mizunami lies about 300 km southwest of Tokyo, about halfway to the Kansai region. Schlee (1990) described amber from this region as being as old as middle Miocene (ca. 15 mya) and as young as

the Pleistocene. Hiura and Miyatake (1974) found arthropods only from the Pleistocene in the samples they studied. A single sample subjected to carbon-14 data analysis yielded an age of 33,000 years, normally indicative of semi-fossilized materials sometimes called copal. Sample 1643 as received in fact was labeled "copal," a term reserved for younger or less mature fossilized resins.

   Sample 1643 was very dark red, nearly black, unusual for Japanese amber. Figure 20 illustrates the ^{13}C spectra of the solid, which are quite different from those in the other figures.
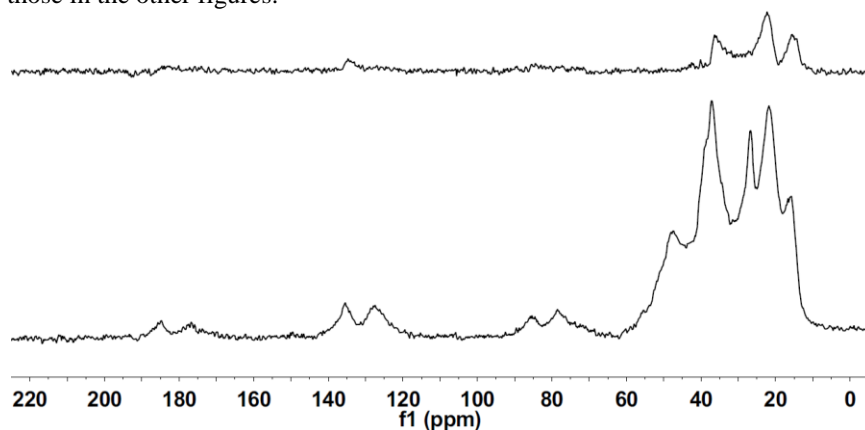

Figure 20. The solid state ^{13}C spectrum of sample 1643 from Mizunami, Gifu Prefecture, with normal decoupling (lower) and with dipolar dephasing (upper).

   Carbon-13 spectra of Group B ambers have been published for samples from Arkansas in the United States (Figure 5 in Lambert et al. 2008), Australia (Figure 1 in Lambert et al. 1993; N.B. these materials were called Group G in this early publication), and Indonesia (Figure 2 in Lambert et al. 2013). Materials from this worldwide group also have been found in other parts of the United States, in Papua New Guinea, and in South Asia (Lambert et al. 1993 and unpublished). The ^{13}C spectrum with full decoupling has strong peaks in the saturated region and weaker peaks in the unsaturated region (Figure 20). The five-peak pattern in the saturated region is diagnostic for Group B, although sometimes the peak at lowest frequency (ca. δ 17) appears only as a shoulder. The spectrum with interrupted decoupling characteristically has three major peaks in the saturated region for Group B materials.

   The solution-phase 1D proton spectrum (Figure 21) is even more highly diagnostic, as it is similar to the numerous spectra of Indonesian amber (Lambert et al. 2013). In particular, spectra of Group B ambers or copals have a doublet at δ 5.5, only a single major set of peaks in the saturated region at δ ca. 0.9, and a characteristic pattern around δ 2.0. Aromatic resonances generally are absent in the region δ ca. 7. The 2D COSY spectrum of sample 1643 (Figure

22) contains two of the four cross peaks that are characteristic of Group B, at 1.6/3.3 and 1.9/5.2 (Lambert et al. 2008 and 2012).
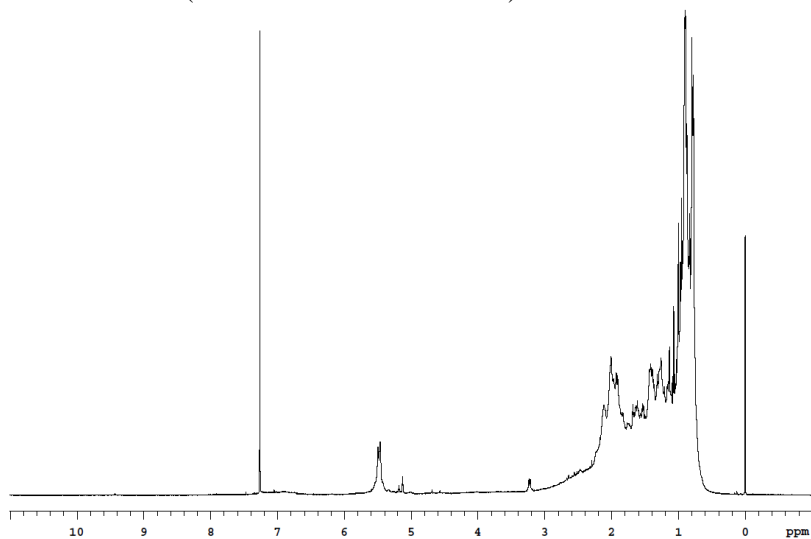

Figure 21. The 1D ^{1}H spectrum of sample 1643 from Mizunami, Gifu Prefecture, in chloroform-*d*.
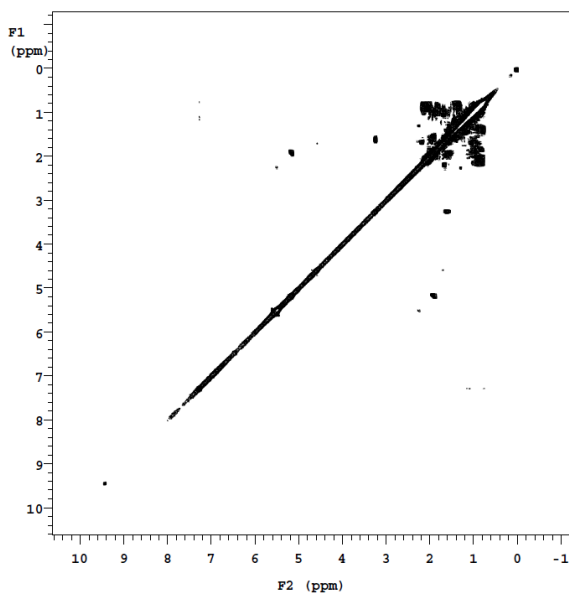

Figure 22. The 2D COSY spectrum of sample 1643 from Mizunami, Gifu Prefecture, in chloroform-*d*.

Summary and Conclusions

Japan has many rich sources of amber and of less fossilized materials derived from plant resins. We have examined 15 Japanese samples from nine different sources extending from the northern island of Hokkaido to the southern tip of the main island of Honshū.   Fourteen of these samples gave the characteristic ^{13}C and ^{1}H spectra of the phenomenological NMR Group A (corresponding to the mass spectral Class Ib), which derive from conifer sources such as Araucariaceae trees. For the most part, the ^{13}C spectra (Figures 2, 11, 12, 14) indicate relatively mature samples, with spectra resembling those from China, Siberia (Figure 4), North America (Figure 3), Western Europe, and Southwest Asia. The ^{13}C spectrum of sample 1646 from Kōsei-chō in Shiga Prefecture (Figure 15), however, exhibits more fine structure in the saturated region and contains resonances from exomethylene carbons at δ ca. 110 and 150.   Such patterns normally are indicative of younger or less fully mature samples. The ^{1}H spectra follow the same pattern. The 1D ^{1}H spectra (Figures 5, 13, and 16) show a range of behavior within that expected for Group A, as do the 2D spectra (Figures 6 and 17). The ^{1}H spectra of sample 1646 (Figures 18 and 19) are richer, again suggestive of younger materials.

Most surprisingly, sample 1643 from Mizunami, Gifu Prefecture, proved to belong to the angiospermous (flowering plant) Group B (mass spectral Class II). Both the ^{13}C (Figure 20) and the ^{1}H (Figures 21 and 22) spectra clearly followed Group B behavior.   Thus, Japan had ancient forests of at least two distinct botanical types that produced resin that led to amber, but the coniferous forests dominated.

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