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Research Article

2-methyl-3-buten-2-ol: A Pheromone Component of Conifer Bark Beetles Found in the Bark of Nonhost Deciduous Trees

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Volatiles from bark of aspen, *Populus tremula* L. and two species of birch: silver birch (*Betula pendula* Roth.) and common birch (*B. pubescens* Ehrh.), were collected by direct solvent extraction and aeration of both newly cut bark chips and undamaged stems in June 1998 and subjected to GC-MS analysis. The results showed the presence of 2-methyl-3-buten-2-ol (MB), one of the two principal aggregation pheromone components of the spruce bark beetle, *Ips typographus*, in bark extraction samples of all the three deciduous tree species tested. In addition, one more oxygenated hemiterpene, 3-methyl-3-buten-2-one, and (*E*)-3-penten-2-ol were also found in the bark extracts. Only trace amounts of MB were detected in some aeration samples of the fresh bark chips, and no MB was found from the aeration samples of undamaged stems at detectable levels. The occurrence of this compound was also confirmed in the bark of four exotic birch species: *B. albosinensis* Schneid., *B. ermanii* Cham., *B. jacquemontii* Spach, and *B. maximowicziana* Regel, but not yet in the European pines/spruces and the common yeasts. Our results raise major questions regarding the evolution, the tropospheric chemistry, and the ecological role of this hemiterpene alcohol. They also suggest that comparative studies on the biosynthetic pathways for MB in different sources would be of considerably evolutionary interest.

1. Introduction

Aspen, *Populus tremula* L. and two birch species, silver birch (*Betula pendula* Roth.) and common birch (*B. pubescens* Ehrh.), are the most common deciduous trees in Norway spruce forests of Scandinavia [1]. Studies showed that volatiles from leaves and bark of nonhost aspen/birch trees strongly inhibit pheromone attraction in spruce bark beetles, *Ips typographus* L. and *Pityogenes chalcographus* L. [2, 3]. In order to determine what kind of volatiles are responsible for the inhibition effect, volatiles from these nonhost trees were collected by headspace aerations and solvent extraction and analyzed by GC-MS [1, 4, 5]. Further electrophysiological and field bioassay studies showed that green leaf alcohols (GLVs) from leaves and bark and some specific compounds like *trans*-conophthorin, from bark of the nonhost deciduous trees, disrupt the secondary attraction response of sympatric coniferophagous bark beetles [4, 5]. Such inhibitory effects by angiosperm nonhost volatiles have been shown on many other conifer-inhabiting bark beetles throughout the world [3]. In the present paper, we report our finding of 2-methyl-3-buten-2-ol (here abbreviated as MB [6], while in atmospheric chemistry often as MBO), one of the principal aggregation pheromone components of *I. typographus,* in the bark of its nonhost trees *P. tremula, B. pendula*, and *B. pubescens*, which poses questions regarding the evolution and ecological role of this semiochemical in the natural habitat.

2. Materials and Methods

Volatiles from the nonhost bark were collected by direct extraction with diethyl ether and by aerations of both newly cut bark chips and undamaged stems in June 1998, Asa, Småland, Sweden. One cm^2 of bark cut into 2×5 mm pieces taken at 1.5 m height of standing trees from each species was extracted in 1 mL of diethyl ether. Fresh bark chips (size: 3×6 cm, with total area of ca. 1000 cm^2) from each individual tree at breast height were aerated in the laboratory within 15–30 min after bark sampling. They were enclosed in a plastic-cooking bag (35 × 43 cm) with an activated charcoal filter tube at the air inlet. The volatiles in the bag were trapped on Porapak Q (30 mg, mesh 50–80 (Supelco), in Teflon tube: ID 3 mm × 35 mm) for 2 h at airflow rate of 300 mL/min and recovered by extraction with diethyl ether [1]. The same aeration setup was also used for the volatile collection from the undamaged stems at 1.3–1.7 m height for 1.5 h with battery-operated pumps. Air temperatures inside and outside of sampling bags were recorded during the aerations with a Min-Max reading thermometer. Additional fresh bark extraction samples of four exotic birch species, *B. albosinensis* Schneid., *B. ermanii* Cham., *B. jacquemontii* Spach, and *B. maximowicziana* Regel, using the same sampling approach as described previously for the three native Scandinavian species were taken from the Alnarp Botanical Garden, Skåne, Sweden in February 1999. All extracts were kept at −20°C before the GC-MS analysis. After collection, the bark samples were dried at 65°C for 72 h and weighed. The detailed information about the bark sampling is shown in Table 1.

The chemical analyses were made by a combined HP 5890 series II gas chromatography and HP 5972 mass selective detector (GC-MSD). The GC was equipped with a 25 m × 0.25 mm × 0.30 μm fused silica column, coated with CP-Wax no. 58 (FFAP CB) (Agilent Technologies). All samples were injected by a HP 7673 autoinjector (2 μL each). Helium was used as the carrier gas at an electronically controlled constant flow of 31 cm/s. The injector temperature was 200°C, and oven temperature was at 30°C for the first 3 min, then programmed to 200°C at 10°C/min, where it remained for 2 min.

Volatiles were identified by comparison of the retention indices and mass spectra with those of authentic compounds, with computerized data library, NBS75K, and with custom produced library (KE1995). Absolute amounts were obtained by comparison to the internal standard, the stabilizer, butylated hydroxytoluene (BHT) of diethyl ether.

3. Results

GC-MS analyses of bark solvent extracts clearly showed the presence of 2-methyl-3-buten-2-ol (MB) in the bark of all the three native Scandinavian deciduous tree species tested (Figure 1). This identification was proven by comparison of retention time and mass spectrum to the authentic compound and computer data libraries (NBS75K and KE1995) (Figure 1). The amounts of MB in the extracts were estimated ca 4.5, 2.5, and 10.7 μg/g dw, for *B. pendula*, *B. pubescens* and *P. tremula*, respectively (Table 2). In addition to the MB, one more oxygenated hemiterpene, 3-methyl-3-buten-2-one, and (*E*)-3-penten-2-ol were identified in the bark extracts, with their average amounts being lower than that of MB (Table 2). The occurrence of MB as a minor component was also confirmed in the bark samples of four exotic birch species: *B. albosinensis*, *B. ermanii*, *B. jacquemontii*, and *B. maximowicziana* by GC-MS.

GC-MS analyses of some aeration samples of the fresh bark chips did also indicate the presence of MB, but only in trace amounts which might be due to the major breakthrough of this highly volatile alcohol through the Porapak Q trap [7]. No MB was found in the aeration samples of undamaged stems at detectable levels.

4. Discussion

4.1. Insect Sources. MB was first identified as one of the principal aggregation pheromone components of spruce bark beetle, *Ips typographus* [8], and was also observed in emissions from the entrance holes made by this species on the trunks of both live [7] and cut [9] spruce trees [10], with emission rates per bore hole being significantly larger than the average content of hindgut. It has been reported as a pheromone component or male-specific compound of several other conifer bark beetles in Eurasia, *Ips* (*Orthotomicus*) *erosus* Woll. [11], *I. nitidus* Eggers [12], *I. shangrila* Cognato and Sun [13], *Pteleobius vittatus* (F.) [14], and *Pityogenes* spp. [15]. MB was found to be produced by females of *Ips amitinus* (Eichhoff) as well and seemed to be inhibitive [16]. It is reportedly an alarm pheromone of the European hornet, *Vespa crabro* L. [17].

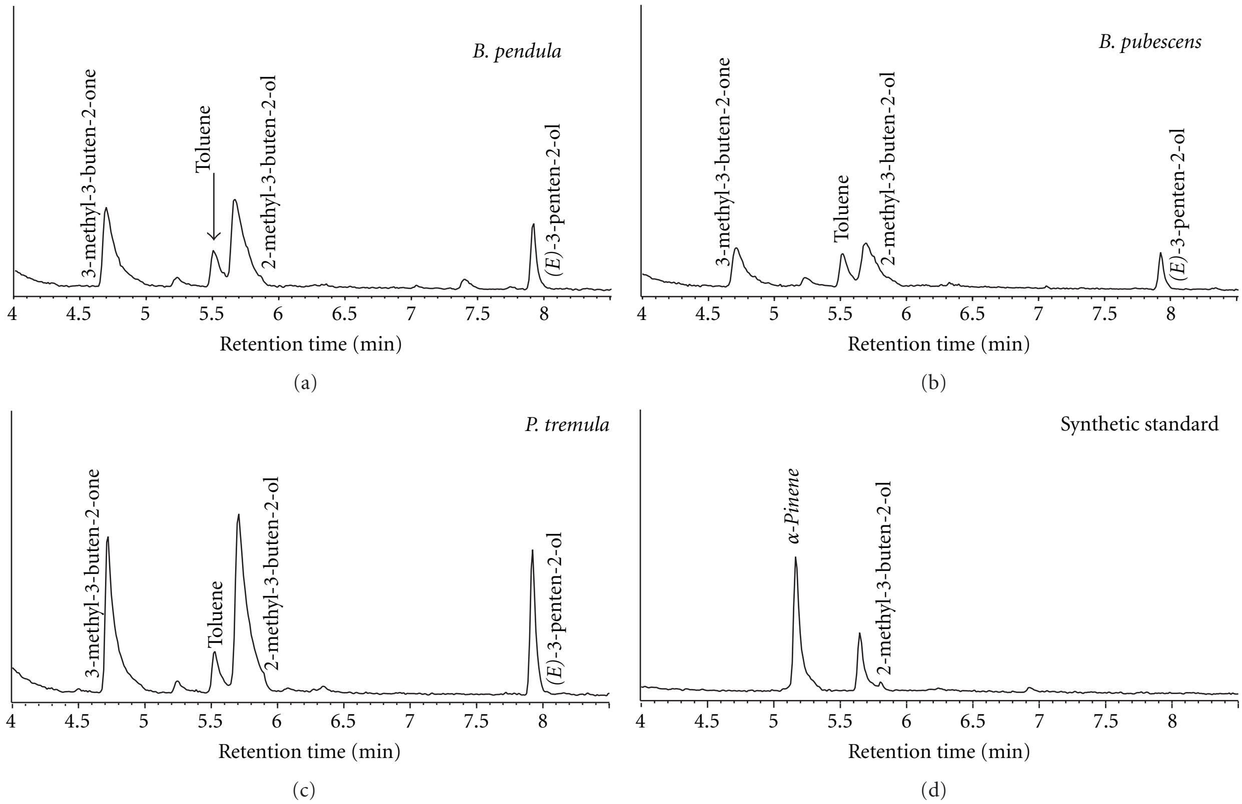
4.2. Plant Sources. This is the first report on the presence of MB in bark of deciduous trees. In addition to the three major native angiosperm deciduous tree species (*P. tremula*, *B. pendula*, and *B. pubescens*), MB was also detected in bark samples (taken in February) of several exotic birch species, including *B. albosinensis*, *B. ermanii*, *B. jacquemontii* and *B. maximowicziana*. Thus, its natural occurrence in plants might be much more common than we ever realized. In fact, the emission of this isoprene alcohol from plants had been observed before; the orchid *Aerides lawrenceae* produces MB [18]. Interestingly, MB is also a hop constituent with sedative hypnotic activity [19] and formed from humulones and lupulones by reaction with OH radicals in the presence of atmospheric oxygen [20]. Further study suggested that the same reaction with OH radicals may occur *in vivo*. For instance, it induced the murine cytochrome P4503A and ethylmorphine N-demethylation (a functional marker for P4503A) in mice [21]. Both 2-methyl-3-buten-2-ol (MB) and 3-methyl-3-buten-2-one are parts of volatile composition from the headspace of five lima bean plants infested with two-spotted spider mites (*Tetranychus urticae* Koch) [22]. MB is also a fragrance ingredient used in cosmetics, fine fragrances, shampoos, toilet soaps, and other toiletries as well as in noncosmetic products such as household cleaners and detergents [23].

Zimmerman et al. (1991) noted the presence of MB in samples taken from enclosures placed around branches of Loblolly pine (*Pinus taeda* L.) [24]. Goldan et al. (1993) characterized the trace gas composition of ambient air in a small clearing in a predominantly lodgepole pine forest with a significant admixture of aspen and occasional Colorado blue spruce (3050 m elevation) in Colorado in June 1991 [25]. They found MB to be the dominant volatile organic compound (VOC), with a concentration 4–7 times higher than that of isoprene. Based on the fact that diurnal changes in

Table 1: Background information on bark samples of nonhost deciduous trees, Sweden.

Samples		Location	Date	Time	No. of trees	Tree dimension		Dry weight or sampling area	Temperature (inside/outside) °C
Scientific name	Common name					Height (m)	DBH (cm)		
Bark extractions of the key species									
B. pendula Roth	Silver Birch	Asa, Småland	1998-06-11	15:00–15:10	2	10–13	10–14	0.16–0.20 g	
B. pubescens Ehrh.	Downy Birch	Asa, Småland	1998-06-11	15:35–15:50	3	12–20	10–18	0.13–0.26 g	
P. tremula L.	Aspen	Asa, Småland	1998-06-11	15:10–15:25	3	8.5–9.0	8–10	0.13–0.20 g	
Bark extractions of additional birch species									
B. albosinensis var. *septentrionalis* Schneid.	Northern Chinese red birch	Alnarp, Skåne	2/24/1999	10:00–10:20	2	9–12	8–12	NA*	
*B. ermanii*Cham.	Erman's birch	Alnarp, Skåne	2/24/1999	10:21–10:40	2	8–10	8–11	NA	
B. jacquemontii Spach	White barked Himalayan Birch	Alnarp, Skåne	2/24/1999	10:41–10:55	2	8–14	7–12	NA	
B. maximowicziana Regel	Monarch Birch	Alnarp, Skåne	2/24/1999	11:10–10:25	2	15–20	15–22	NA	
Aerations of fresh bark chips									
B. pendula Roth	Silver Birch	Asa, Småland	1998-06-09	9:30–10:00	4	13–16	14–16	147–152 g	21.9–22.7/21–21.7
B. pubescens Ehrh.	Downy Birch	Asa, Småland	1998-06-08	17:00–17:30	4	15–20	24–30	140–210 g	22.8–23.4/22.5–23
P. tremula L.	Aspen	Asa, Småland	1998-06-09	9:30–10:00	4	12–17	11–20	106–194 g	21.9–22.7/21–21.7
Aerations of undamaged stems									
B. pendula Roth	Silver Birch	Asa, Småland	1998-06-29	12:50–14:20	2	15–20	18–20	0.22–0.24 m^2	17.5–31.4/15.5–21.3
B. pubescens Ehrh.	Downy Birch	Asa, Småland	1998-06-29	13:55–15:25	2	15–20	12–20	0.11–0.16 m^2	19.5–20.0/18.3–19.2
P. tremula L.	Aspen	Asa, Småland	1998-06-29	12:15–13:45	2	13–15	14–18	0.18–0.22 m^2	17.5–31.4/15.5–21.3

*No fresh/dry weights were measured, and the amounts of 232 MB in the samples were not quantified.



(a) (b) (c) (d)

Figure 1: Gas chromatograms from bark extracts of *B. pendula, B. pubescens*, and *P. tremula,* and synthetic standard of 2-methyl-3-buten-2-ol (MB).

Table 2: Amounts of oxygenated hemiterpenes and (*E*)-3-penten-2-ol present in the bark extracts of deciduous trees, Asa, Sweden, June 11, 1998.

Compounds	Mean ± SD (μg/g DW bark)		
	B. pendula ($n = 2$)	*B. pubescens* ($n = 3$)	*P. tremula* ($n = 3$)
2-methyl-3-buten-2-ol (MB)	4.53 ± 1.37	2.51 ± 2.80	10.68±5.63
3-methyl-3-buten-2-one	3.83 ± 1.13	1.66 ± 2.06	7.42 ± 4.33
(*E*)-3-penten-2-ol	1.37 ± 0.46	0.61 ± 0.81	4.04 ± 2.02

ambient MB concentrations were very similar to those of isoprene, with known biogenic sources, and on the fact that MB concentrations did not correlate well with those of benzene, an indicator of anthropogenic source, they concluded that there was likely to be a large local biogenic source of MB, probably the lodgepole pine forest. Harley et al. (1998) successfully detected and measured the emission of MB from needles of several North American pine species, confirming MB as a biogenic VOC (BVOC) [26]. MB emissions from *Pinus ponderosa* were absent in the dark and strongly dependent on incident light, behaving similarly to net photosynthesis. The fact that MB emissions rapidly fall to near zero in darkness suggested that MB is being emitted immediately upon production, rather than stored in any specialized structures of pine needles. Their further screening study on 34 species of pines for MB emission in California showed that 11 species exhibited high emissions of MB (>5 μg C/g/h), and 6 emitted small but detectable amounts. All the emitting species are of North American origin, and most are restricted to western North America. Their results from both intact and severed branches indicated that MB emissions from pines may constitute a significant source of reactive carbon and a significant source to the atmosphere of acetone, a product of MB oxidation [26]. Interestingly, we find no MB records from European pines, and MB is not detected, based on its characteristic base ion $m/z = 71$, in the host tree *Picea abies* L. neither from bark extracts (C. Schiebe, unpubl.) nor emitted from foliage (M. Binyameen, unpubl.).

4.3. Microbial Sources. A plethora of short-chained BVOC is produced by yeasts and other microorganisms, including methyl butenol isomers [27, 28]. Somewhat surprisingly, the insect- and plant-produced 2-methyl-3-buten-2-ol is not reported in the microbial-related literatures, and is not found among VOCs analyzed with GC-MS from different types of cultured yeasts (M. Proffit, unpubl results).

4.4. Atmospheric Chemistry. Following the observation of MB emission in pine forest by Goldan et al. (1993) [25], several studies on the atmospheric chemistry of this BVOC alcohol have been actively carried out [29–35]. Harley et al. (1998) claimed that the major photochemical sink for MB during daylight hours is assumed to be with OH^- [26]. The rate coefficients with similar values for the OH^- reaction with MB were reported by Rudich et al. (1995) and Ferronato et al. (1998), which suggested a relatively short atmospheric lifetime of ca. 2 hours [30, 34]. However, given typical atmospheric values of O_3 and NO_3, the rate constants for MB reaction with O_3 [32] or with NO_3 [33, 34] imply significantly longer MB lifetimes with respect to these destruction processes. Further reaction chamber experiments [29, 30] indicate that the MB–OH reaction leads to the production of acetone, glycol aldehyde, formaldehyde, and presumably 2-hydroxy-2-methylpropanal. The reaction with O_3 appears to yield the same major products, though in different proportions [29, 32]. Recently, Chan et al. (2009) suggested that photooxidation of MB might be a potential but minor source of secondary organic aerosol (SOA) [35]. Despite its structural similarity to isoprene, photooxidation of MB is not expected to make a significant contribution to SOA formation [35].

By using a model considering landscape average emission potential (μg C $g^{-1} h^{-1}$), total foliar density (g m^{-2}) (estimated by the available data on forest biomass and species composition), and emission activity factor, Harley et al. (1998) were able to compare the ambient concentrations of MB observed by Goldan et al. (1993) with their own enclosure rates of MB emission and found a reasonable agreement [25, 26]. Recent estimate of global MB emission is about 9.6 Tg per year [36, 37].

4.5. Potential Semiochemical Functions. MB seems to have multiple functions, including semiochemical, flavor, and pharmacological roles, and strong impact on atmospheric chemistry, which are dependent on its sources. The role of MB in the semiochemical system of *I. typographus* has been intensively studied. On the basis of dose-response curves from electroantennograms (EAGs), Dickens (1981) suggested that MB might act as a close-range/landing substance as it had a higher threshold (100 μg on filter paper) and very steep dose-response profile [38]. By using specially designed trap groups, Schlyter et al.(1987) clearly showed that MB does act as a close-range landing (or entering of trap holes) stimulus in the field [39]. However, our combined gas chromatographic-electroantennographic detection (GC-EAD) analysis of the bark extract samples of these three tree species showed no antennal responses by *I. typographus* to the existing MB (Zhang et al. unpubl.). It is mainly due to the fact that the amounts of MB in the extracts are much lower than the response threshold of *I. typographus* [38]. Furthermore, no MB was detected in the aeration samples of the undamaged stems, which might be caused by either the breakthrough of this compound through the Porapak Q trap or the minor amounts of release. Thus, the amounts of MB produced by the bark of nonhost birch or aspen, or emitted from the undamaged stems if any, most probably have no significant impact on the host selection behavior of *I. typographus* in the natural habitat. Goldan et al. (1993) doubted the source of MB from *I. typographus* and speculated an extra-insect source from host spruce trees [25]. In contrast, our GC-MS analyses of aeration samples of bark chips and cut branches with fresh needles of Norway spruce, *Picea abies*, did not find any MB at detectable levels [1]. In fact, no MB emitting trees had been discovered in Europe where the two bark beetles (*I. typographus* and *Ips* (*Orthotomicus*) *erosus*) use MB as parts of their pheromone systems prior to our current study.

Inclusion of MB in a trap consisting of a mixture of pheromone attractants for the spruce bark beetle, *Dendroctonus rufipennis*, was shown to reduce the number of *D. rufipennis* trapped, suggesting a possible antiattractant role of this alcohol [40]. However, MB exhibited no repellent properties when tested alone nor did it appear to have any effect on the aggregation response of two North American conifer bark beetles (*Ips paraconfusus* and *Dendroctonus brevicomis*) and their predators (Trogositidae and Cleridae) to their pheromones [41].

4.6. Biosynthesis. A biosynthetic study by Lanne et al. (1989), using radiolabeled precursors, clearly showed that MB is produced *de novo* by *I. typographus* through the mevalonic pathway [9]. The biosynthetic pathway in other insects (*Ips* (*Orthotomicus*) *erosus*, *I. nitidus* and *I. shangrila*, and *Vespa crabro*) and the Eurasian angiosperm trees (bark of birch and aspen) still remains unknown. However, the gene for MB synthase was recently identified from *Pinus sabiniana*, the MB producing pine species, and the protein encoded was functionally characterized by Gray et al. (2011) [42]. MB synthase is a bifunctional enzyme which produces both MB and isoprene in a ratio of ca. 90 : 1 [42] via dimethylallyl diphosphate (DMADP) [43]. Another oxygenated hemiterpene, 3-methyl-3-buten-2-one, was also found constantly from our bark extracts. It is not clear if this oxygenated hemiterpene is involved in the biosynthetic pathway of MB. Our results raise major questions regarding the evolution, tropospheric chemistry, and ecological role of this short, branched alcohol. They also suggest that comparative studies on the biosynthetic pathways for MB in different natural sources would be of considerable evolutionary interest.

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