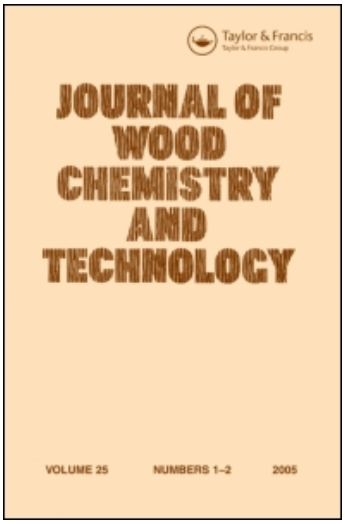

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TRITERPENOID CONSTITUENTS IN THE OUTER BARK OF *BETULA ALLEGHANIENSIS* (YELLOW BIRCH)

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ABSTRACT

Yellow birch, *Betula alleghaniensis*, is a dark-barked birch species that is widely utilized in the northeastern region of the United States for pulp and solid wood products. Currently, the bark is used only as a low value fuel source. In this study, the triterpenoid composition of the outer bark of *B. alleghaniensis* was investigated in order to evaluate potential for use as a resource for specialty chemicals. Seventeen triterpenoids, including four new compounds, were isolated and identified. Previously known compounds included lupeol, lupenone, betulone, betulin, betulonic acid, lupenyl formate, lup-20(29)-ene-30-ol-3-one, lup-20(29)-ene-3β,30-diol, lup-20(29)-ene-28-ol-30-al, 29-norlupan-3β-ol-20-one, lupan-20-ol-3-one, lupan-3β,20-diol, and lupan-3β-ol-29-oic acid. The four new compounds isolated from yellow birch were lup-20(29)-ene-28-ol-3-one-30-al, 29-norlupan-3,20-dione, 29-norlupan-28-ol-3,20-dione, and lupan-20,28-diol-3-one.

INTRODUCTION

Yellow birch (*Betula alleghaniensis* or *B. lutea*) is a commercially important hardwood species in the eastern region of

the United States. The wood is commonly used for furniture, flooring, and cabinetry. It has been estimated that about three-fourths of the lumber marketed as "birch", approximately 145,000,000 board feet per year, is yellow birch[1]. It is also a preferred pulp species because of its long fiber length. Such widespread utilization of this species generates a vast quantity of waste bark which currently is used only as a fuel for energy production. The utilization of this bark for higher value products is thus a subject of considerable interest. In order to adequately evaluate potential uses of the bark, it is necessary to investigate the composition of the bark.

It has been well established that the outer bark of most white-barked birch species are rich in pentacyclic triterpenoid compounds, particularly betulin. In studies of the European birch species, *B. verrucosa* and *B. pubescens*, it was found that the barks contained up to 40%, by weight, total triterpenoids with betulin alone comprising up to 35% of the weight of the outer bark[2]. Such unusually high levels of a single component make the bark an especially attractive resource for further utilization.

While the barks of European and Japanese birch species have been thoroughly investigated[2-9], little is known regarding the composition of the barks of species native to the United States. In a previous study in our laboratory, we determined that betulin was the major triterpenoid component in the outer barks of four native white-barked species: *B. papyrifera* (paper birch), *B. populifolia* Marsh. (gray birch), *B. cordifolia* Regel. (mountain paper birch), and *B.* X *caerulea* Blanch. (blue birch). In these species, betulin comprised 6-22% of the outer bark and contributed about 75% of the triterpenoid content. Lupeol was the second most abundant triterpenoid, accounting for 0.2-2%, by weight, of the bark[10].

In addition to the white-barked species discussed above, two dark-barked birch species also are native to the northeastern U.S. In an earlier study[11], we analyzed the outer bark of black birch and found that the triterpene composition was significantly different than that observed in the white-barked species. The total triterpene

content was considerably lower, approximately 0.8%, in black birch and lupeol was the predominant triterpene, representing about 60% of the total triterpenes. Betulin was present at lower levels, comprising approximately 35% of the triterpene content.

As was the case with black birch, almost no research has been conducted regarding the triterpenoid composition of the bark of the abundant and commercially important dark-barked species, *Betula alleghaniensis* (yellow birch). In the only previous study of this species, Seshadri and Vedantham[12] found lupenone to be the primary triterpenoid with trace amounts of betulin and lupeol present also.

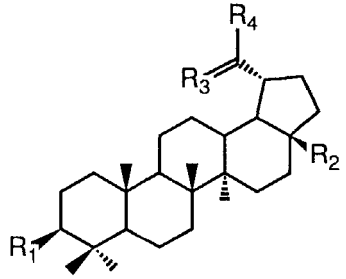
This paper reports the findings of a thorough investigation of the triterpenoid composition of the outer bark of *B. alleghaniensis*.

RESULTS AND DISCUSSION

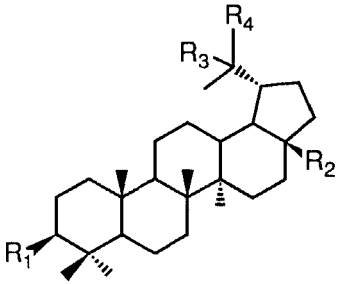
A total of seventeen triterpenoid components were isolated and identified from the outer bark of yellow birch (Table 1). The total amount of triterpenes was 3.5%, based on the dry weight of bark, which was significantly lower than the levels observed in the white-barked species, but much higher than the 0.8% total triterpenes found in black birch.

Lupeol (**I**) was the major triterpenoid compound in yellow birch, as it was in black birch, comprising approximately 45% of the total triterpenes. The remainder of the terpene composition, however, was quite unique. Lupenone (**II**) was the second most abundant compound (28%). Both lupeol and lupenone are well known components of birch barks, but the high relative abundance of lupenone in yellow birch has not been observed in other species. Lup-20(29)-ene-28-ol-3-one (betulone) (**III**) was also present at surprisingly high levels (13.7% of total triterpenes). This compound was first isolated and identified as a natural product in our earlier study of

TABLE 1. Triterpenoid Compounds in *Betula alleghaniensis*.



	R_1	R_2	R_3	R_4	Name
I	β-OH	CH_3	CH_2	CH_3	lupeol
II	=O	CH_3	CH_2	CH_3	lupenone
III	=O	CH_2OH	CH_2	CH_3	betulone
IV	β-OH	CH_2OH	CH_2	CH_3	betulin
V	=O	CO_2H	CH_2	CH_3	betulonic acid
VI	HCO_2	CH_3	CH_2	CH_3	lupenyl formate
VII	=O	CH_3	CH_2	CH_2OH	lup-20(29)-ene-30-ol-3-one
VIII	β-OH	CH_3	CH_2	CH_2OH	lup-20(29)-ene-3β,30-diol
IX	=O	CH_2OH	CH_2	CHO	lup-20(29)-ene-28-ol-3-one-30-al
X	β-OH	CH_3	CH_2	CHO	lup-20(29)-ene-3β-ol-30-al
XI	β-OH	CH_3	O	CH_3	29-norlupan-3β-ol-20-one
XII	=O	CH_3	O	CH_3	29-norlupan-3,20-dione
XIII	=O	CH_2OH	O	CH_3	29-norlupan-28-ol-3,20-dione



	R_1	R_2	R_3	R_4	Name
XIV	=O	CH_3	OH	CH_3	lupan-20-ol-3-one
XV	β-OH	CH_3	OH	CH_3	lupan-3β,20-diol
XVI	=O	CH_2OH	OH	CH_3	lupan-20,28-diol-3-one
XVII	β-OH	CH_3	H	CO_2H	lupan-3β-ol-29-oic acid

black birch and was found to comprise approximately 1% of the triterpenoid content in that species[11].

The next most abundant compound in yellow birch was lupan-20-ol-3-one (**XIV**), which accounted for 7.9% of the triterpene content. **XIV** was first isolated from the stems of *Lithocarpus polystachya*[13] and later from *Pleurostylia opposita*[14], but it has not been isolated from a birch species. Yellow birch contained only a small amount of betulin (**IV**) in the outer bark,comprising only 2.6% of the total triterpenes, which corresponds to 0.09% of the bark. This is in sharp contrast to the white-barked species in which betulin made up 8-40% of the weight of the outer bark. Only one other compound, lupan-3β,20-diol (**XV**), was present at a significant level (1.7%) in the yellow birch extract. This compound, also known as monogynol A, was isolated from black birch in trace quantities[11] and has been reported in *Betula verrucosa*[2,3] and *B. maximowicziana*[15].

The remaining triterpenoid components that were isolated and identified were each present at a level of less than 1% of the total triterpenes. These included betulonic acid (**V**), which was isolated in a trace amount from the bark of *Betula verrucosa*[2] and from the Sri Lankan *Glochidion* species[16], and lupenyl formate (**VI**), which previously has been observed only in pokasa bark[17]. Two compounds, lup-20(29)-ene-30-ol-3-one (**VII**) and lup-20(29)-ene-3β,30-diol (**VIII**), which contain hydroxyl groups at the 30 position, also were present at trace levels in yellow birch. **VII** was isolated first from *Flourensia heterolepsis*[18] and later was identified in the bark of the Sri Lankan shrub, *Gymnosporia emarginata*[19]. Compound **VIII**, which is the lupeol analog of **VII**, appears to be more common, having been isolated from several sources including the stems of *Lithocarpus polystachya*[13], the bark of *Lawsonia inermis*[20], and the leaves of *Catha cassinoides*[21]. In addition, **VIII** was isolated from the outer bark of *Betula lenta*[11].

Compounds **IX**, lup-20(29)-ene-28-ol-3-one-30-al, and **X**, lup-20(29)-ene-3β-ol-30-al, both contain aldehyde groups at the 30 position. Whereas **X** has been isolated from several sources including the

stems of *Lythocarpus polystachya*[13] and the leaves of *Ilex cornuta* Lindl.[22], **IX** is, to our knowledge, a new compound. Our assignment of this compund to lup-20(29)-ene-28-ol-3-one-30-al was based on ^{1}H-NMR, IR, MS, and high resolution MS data, as well as comparison of spectral data with similar known compounds. A crystalline product was not obtained and thus a melting point could not be determined.

Three norlupane derivatives (**XI, XII,** and **XIII**), in which the 29 carbon was cleaved, also were present in the outer bark of yellow birch. While 29-norlupan-3β-ol-20-one (**XI**) is a well known natural product [13,20,23-25], 29-norlupan-3,20-dione (**XII**) and 29-norlupan-28-ol-3,20-dione (**XIII**) are new compounds. Spectroscopic evidence indicated that these compounds were closely related to **XI**, differing only in the substituents at positions 3 and 28. **XII** has a ketone group at C-3 as evidenced by the absence of the H-3α signal at δ3.18 in the ^{1}H-NMR and the presence of a signal at δ217.8 for C=O in the ^{13}C-NMR spectrum. The ^{1}H-NMR of **XII** was identical to that of the product obtained by ozonolysis of lupenone, further confirming the identification as 29-norlupan-3,20-dione. The ^{1}H-NMR of **XIII** showed methylene doublets at δ3.28 and 3.76, indicating the presence of the 28-hydroxyl group.

Lupan-20,28-diol-3-one (**XVI**) is a new compound also. Although its lupenone analog (**XIV**), differing only at the 28 position, was identified in several other sources in addition to yellow birch, **XVI** has not been isolated from a natural source or synthesized previously. Assignment of this compound to lupan-20,28-diol-3-one is consistent with the spectral data obtained in this study.

The last triterpenoid component isolated in a trace amount from the bark of yellow birch was lupan-3β-ol-29-oic acid (**XVII**). This compound was isolated from *Pseudocyphellaria rubella*[25], but has not been observed in *Betula* species before.

It is interesting to note that, in general, the triterpenoid components present in yellow birch are more highly oxidized than those in black birch. For example, in yellow birch, betulone was much more abundant than betulin, while in black birch the opposite

situation was observed. Similarly, yellow birch contained betulonic acid, with a ketone at the 3 position, whereas black birch contained betulinic acid, in which the 3 substituent is a hydroxyl group. Both species contained lupan-3β,20-diol (**XV**), but two more highly oxygenated derivatives, lupan-20-ol-3-one (**XIV**) and lupan-20,28-diol-3-one (**XVI**), also were present in yellow birch.

EXPERIMENTAL

General Experimental Procedures: IR spectra were recorded on a Digilab FTS-60 spectrometer. ^{1}H-NMR and ^{13}C-NMR were obtained on a Varian XL-200 spectrometer. Low resolution mass spectra were recorded on an HP-5985B mass spectrometer operating at 70 ev. High resolution mass spectra were obtained on a VG-70E system at the Auburn University Mass Spectrometry Facility by Dr. George Goodloe. Uncorrected melting points were determined on a Fisher-Johns melting point apparatus. Individual components were quantified by determining weights of pure compound fractions.

Extraction: Outer bark was collected from trees at a height of 1-1.3 m. Bark was ground in a Wiley mill into particles less than 1mm in diameter and dried to a constant weight at 100°C. 294 g of milled bark were extracted by refluxing in 1.1 L chloroform for 15 minutes. The extract was filtered and the residual bark similarly extracted two more times. The combined extracts were evaporated under vacuum to yield 32.5 g of dry extractives.

Isolation and Identification: A portion of the extract (11.84 g) was chromatographed on silica gel (230-400 mesh, Merck) using hexane followed by a hexane/toluene gradient (20:1-0:100) and a toluene/ethyl acetate gradient (20:1-0:100). Individual compounds were purified by additional column chromatography, preparative thin layer chromatography (Macherey-Nagel, Polygram Sil-G/UV$_{254}$ plates),

and recrystallization. Identifications were based on MS, ^{1}H-NMR, and IR. Spectra were compared to available authentic samples and to literature data.

Compounds **I** (lupeol), **II** (lupenone), and **IV** (betulin) were crystallized individually from 95% EtOH to give white crystalline solids. These compounds were identified by comparison of melting points, ^{1}H-NMR, and MS with authentic samples. 1.7 g lupeol, 1.05 g lupenone, and 100 mg of betulin were isolated.

Compound **III** (lup-20(29)-ene-28-ol-3-one = "betulone") was obtained by preparative TLC using toluene/ethyl acetate (16:4) followed by hexane/ether (1:1). 517 mg of a light yellow oil was obtained. HRMS $[M]^+$ 440.362 calculated for $C_{30}H_{48}O_2$, observed 440.3654. MS m/e (rel. int.) 440 (M^+, 32), 409 (100), 397 (13), 315 (13), 286 (18), 245 (36), 203 (78), 189 (64), 175 (32), 163 (33), 147 (42), 133 (50), 119 (60), 107 (69), 95 (85), 81 (86), 67 (93), 55 (100). IR (NaCl) cm^{-1} 3470 (OH), 1704 (C=O), 1654 (C=C). ^{1}H-NMR ($CDCl_3$, J=Hz) δ: 0.93-1.68 (18H, s, 6 x Me), 2.41 (2H, m, -CO-C<u>H</u>$_2$-), 3.35 (1H, d, J=11), 3.80 (1H, d, J=11). ^{13}C-NMR ($CDCl_3$) δ: 218 (C=O), 150, 109 (C=CH_2), 60 (CH_2OH). APT showed 11 CH_3 and CH carbons and 19 CH_2 and C carbons. Reduction of Compound **III** with $NaBH_4$ gave the known compound, betulin (**IV**).

Compound **V** (betulonic acid) was purified further by preparative TLC using toluene/acetone (14:2) to give 3 mg of a white amorphous solid. MS m/e (rel. int.) 454 (M^+, 23), 430 (25), 408 (15), 248 (100), 235 (38), 219 (44), 205 (78), 189 (95), 177 (85), 161 (32.9), 149 (98), 133 (55), 121 (70), 107 (80), 95 (80), 81 (91), 67 (84), 55 (100), 43 (94). IR (NaCl) cm^{-1} 3400-2500 (COOH), 1710,1720 (C=O, COOH), 1650 (C=C). ^{1}H-NMR ($CDCl_3$, J=Hz) δ: 0.87-1.04 (15H, s, 5 x Me), 1.69 (3H, s, Me-30), 2.46 (2H, m, H-2), 3.00 (1H, m, H-19), 4.62 (1H, m, H-29), 4.75 (1H, m, H-29).

Compound **VI** (lupenyl formate) was purified by preparative TLC using hexane/toluene (2:1) and recrystallized from 95% EtOH to give 1

mg of a white solid, m.p. 236-238°. MS m/e (rel. int.) 454 (M^+, 20), 439 (8), 297 (5), 235 (31), 218 (31), 203 (37), 189 (87), 108 (55). IR (NaCl) cm^{-1} 1738 (ester), 1612 (C=C). ^{1}H-NMR ($CDCl_3$, J=Hz) δ: 0.76-1.69 (21H, s, 7 x Me), 4.57, 4.68 (3H, m, C=CH_2, C<u>H</u>-O-C=O), 8.11 (1H, s, H-formate). Except for the melting point which was reported as 190-192° [17], this spectral data coincides with that in the literature.

Compound **VII** (lup-20(29)-ene-30-ol-3-one) was obtained by preparative TLC using toluene/acetone (17:4). Recrystallization from 95% EtOH yielded 4 mg colorless needles, m.p. 181-182°. MS m/e (rel. int.) 440 (M^+, 38), 422 (13), 407 (9), 382 (10), 313 (58), 245 (25), 234 (13), 221 (38), 205 (100), 189 (32), 175 (20), 163 (38), 149 (38), 135 (40), 121 (58), 107 (75), 95 (81), 81 (71). IR (NaCl) cm^{-1} 3400 (OH), 1706 (C=O), 1610 (C=CH_2). ^{1}H-NMR ($CDCl_3$, J=Hz) δ: 0.79-1.07 (18H, s, 6 x Me), 2.45 (2H, m, H-2), 4.13 (2H, br s, -C<u>H</u>$_2$OH), 4.90, 4.94 (2H, m, C=C<u>H</u>$_2$). This spectral data coincides with reported data [18,19].

Compound **VIII** (lup-20(29)-ene-3β,30-diol) was obtained by preparative TLC using toluene/acetone (17:6). Recrystallization from 95% EtOH yielded 5.3 mg colorless needles, m.p. 236-237°. MS m/e (rel. int.) 442 (M^+, 7), 424 (4), 315 (10), 234 (18), 220 (16), 207 (75), 189 (68), 175 (25), 161 (31), 147 (38), 135 (68), 121 (64), 107 (83), 95 (100), 81 (92), 69 (66), 55 (81). IR (NaCl) cm^{-1} 3345 (OH), 1650 (C=C). ^{1}H-NMR ($CDCl_3$, J=Hz) δ: 0.76-1.03 (18H, s, 6 x Me), 3.19 (1H, m, H-3α), 4.12 (2H, br s, -C<u>H</u>$_2$OH), 4.93 (2H, m, C=C<u>H</u>$_2$). The ^{1}H-NMR signals at δ 3.19 and 4.12 shifted to 4.45 and 4.55, respectively, in the spectrum of the diacetate derivative of this compound. This spectral data coincides with that given by Betancor *et al.* [21].

Compound **IX** (lup-20(29)-ene-28-ol-3-one-30-al) was purified further by preparative TLC using toluene/acetone (14:2) to give 4 mg of an amorphous solid. HRMS $[M]^+$ 454.3435 calculated for $C_{30}H_{46}O_3$, found 454.3433. MS m/e (rel. int.) 454 (M^+, 7), 423 (21), 411 (5), 217 (12), 205 (24), 189 (18), 163 (18), 147 (21), 135 (26), 119 (32), 107 (44), 95 (55), 81 (65), 67 (70), 55 (100), 43 (95). IR (NaCl) cm^{-1} 3470 (OH), 1693 (C=C-CHO), 1610 (C=C), 1117, 1038 (C-O). ^{1}H-NMR ($CDCl_3$, J=Hz) δ:

0.91-1.06 (15H, s, 5 x Me), 2.40 (2H, m, H-2), 3.40 (1H, d, J=11.5, H-28), 3.76 (1H, d, J=11.5, H-28), 5.92 (1H, s, C=C$\underline{H}_2$), 6.28 (1H, s, C=C$\underline{H}_2$), 9.50 (1H, s, CHO).

Compound **X** (lup-20(29)-ene-3β-ol-30-al) was obtained by preparative TLC using toluene/ethyl acetate (16:4). Recrystallization from 95% EtOH yielded 6 mg colorless needles, m.p. 225-226°. MS m/e (rel. int.) 440 (M^+, 15), 422 (11), 407 (9), 379 (4), 232 (12), 218 (14), 207 (43), 203 (48), 189 (70), 175 (24), 161 (28), 147 (30), 135 (50), 121 (55), 107 (68), 95 (80), 81 (90), 67 (85), 55 (100), 43 (98). IR (NaCl) cm^{-1} 3280 (OH), 1690 (CH_2=C-C=O), 1630 (C=C), 1052 (C-O). ^{1}H-NMR ($CDCl_3$, J=Hz) δ: 0.74-1.01 (18H, s, 6 x Me), 3.19 (1H, m, H-3α), 5.90 (1H, s, H-C=C-), 6.28 (1H, s, H-C=C-), 9.51 (1H, s, CHO). This spectral data coincides with that in the literature [22]. This structure was confirmed further by synthesis of **VIII** from lupeol (**I**). Acetylation of lupeol with acetic anhydride in pyridine followed by oxidation with SeO_2 yielded 3-acetyl-lup-20(29)-ene-30-al. Hydrolysis of the acetate group with KOH/MeOH gave Compound **VIII**.

Compound **XI** (29-norlupan-3β-ol-20-one) was obtained by preparative TLC using toluene/acetone 14:2). Recrystallization from 95% EtOH gave 10 mg of a white solid, m.p. 237-239°. MS m/e (rel. int.) 428 (M^+, 9), 410 (14), 385 (4), 367 (8), 248 (10), 234 (10), 207 (37), 189 (60), 175 (23), 163 (21), 147 (24), 135 (37), 121 (38), 107 (45), 95 (54), 81 (51), 67 (47), 55 (50), 43 (100). IR (NaCl) cm^{-1} 3450 (OH), 1701 (C=O), 1050 (C-O). ^{1}H-NMR ($CDCl_3$, J=Hz) δ: 0.76-1.04 (18H, s, 6 x Me), 2.15 (3H, s, CH_3-C=O), 2.58 (1H, m, H-19), 3.18 (1H, m, H-3α). This spectral data coincides with that in the literature [23,24,26].

Compound **XII** (29-norlupan-3,20-dione) was purified further by preparative TLC using toluene/ethyl acetate (16:4) to give 7 mg colorless needles which were recrystallized from 95% EtOH, m.p. 204°. HRMS $[M]^+$ 426.3486 calculated for $C_{29}H_{46}O_2$, observed 426.3484. MS m/e (rel. int.) 426 (M^+, 40), 408 (6), 383 (8), 340 (12), 231 (12), 205 (50), 191 (18), 177 (23), 163 (46), 149 (29), 135 (29), 121 (37), 107

(42), 95 (51), 81 (53), 67 (37), 55 (52), 43 (100). IR (NaCl) cm^{-1} 1704 (C=O). ^{1}H-NMR ($CDCl_3$, J=Hz) δ: 0.77-1.06 (18H, s, 6 x Me), 2.14 (3H, s, CH_3C=O-), 2.43 (3H, m, H-2 and H-19). ^{13}C-NMR ($CDCl_3$) δ: 14.4, 15,7, 16.0, 18.0, 19.7, 21.0, 21.4, 26.7, 27.0, 27.2, 27.6, 29.0, 33.4, 34.0, 34.9, 36.8, 37.1, 39.5, 39.8, 40.6, 42.7, 43.0, 47.2, 49.4, 49.5, 52.5, 54.7, 212.0 (C-20), 217.8 (C-3).

Compound **XIII** (29-norlupan-28-ol-3,20-dione) was obtained by preparative TLC using toluene/ethyl acetate (14:10). Recrystallization from 95% EtOH yielded 3 mg of an amorphous white solid. HRMS $[M]^+$ 442.3447 calculated for $C_{29}H_{46}O_3$, found 442.3445. MS m/e (rel. int.) 442 (M^+, 35), 411 (35), 207 (37), 189 (47), 161 (35), 149 (50), 135 (47), 121 (47), 107 (54), 95 (58), 81 (64), 69 (50), 55 (66), 43 (100). IR (NaCl) cm^{-1} 3430 (OH), 1704 (C=O), 1038 (C-O). ^{1}H-NMR ($CDCl_3$, J=Hz) δ: 0.92-1.07 (15H, s, 5 x Me), 2.16 (3H, s, CH_3C=O), 2.45 (2H, m, H-2), 2.60 (1H, m, H-19), 3.28 (1H, d, J=11.5, H-28), 3.76 (1H, d, J=11.5, H-28).

Compound **XIV** (lupan-20-ol-3-one) was purified by preparative TLC using toluene/acetone (17:4) and recrystallized from 95% EtOH to give 300 mg of colorless needles, m.p. 210-212°. MS m/e (rel. int.) 424 (M^+-H_2O, 19), 409 (9), 384 (9), 218 (15), 205 (43), 189 (22), 163 (18), 149 (28), 135 (22), 121 (30), 107 (33), 95 (43), 81 (43), 59 (100). IR (NaCl) cm^{-1} 3460 (OH), 1694 (C=O). ^{1}H-NMR ($CDCl_3$, J=Hz) δ: 0.82-1.23 (24H, s, 8 x Me), 2.43 (2H, m, -CH_2-C=O). ^{13}C-NMR ($CDCl_3$) δ: 218.0 (C-3). This spectral data coincides with that reported in the literature[13,14,27].

Compound **XV** (lupan-3β,20-diol = monogynol A) was purified further by preparative TLC using toluene/ethyl acetate (1:1). Recrystallization from 95% EtOH gave 63 mg of colorless needles, m.p. 240-242°. MS m/e (rel. int.) 426 (M^+ - H_2O, 41), 411 (16), 386 (12.5), 257 (10), 229 (18), 218 (58), 207 (78), 189 (100), 175 (38), 161 (36), 149 (56), 135 (74), 121 (66), 107 (74), 95 (87), 81 (74), 59 (88). IR (NaCl) cm^{-1} 3300 (OH). ^{1}H-NMR ($CDCl_3$, J=Hz) δ: 0.76-1.22 (24H, s, 8 x Me), 3.19 (1H, br s, H-3α). ^{13}C-NMR showed two oxygenated carbons, δ

79.024 and 73.524. Acetylation of this compound with acetic anhydride/pyridine yielded the monoacetate: ^{1}H-NMR ($CDCl_3$, J=Hz) δ: 0.78-1.22 (24H, s, 8 x Me), 2.04 (3H, s, CH_3CO_2-), 4.47 (1H, m, H-3α). The structure of this compound was confirmed further by reduction of the known compound, lupan-20-ol-3-one, with $NaBH_4$ in dioxane for 2.5 hours. The ^{1}H-NMR of the reduction product was identical to that of Compound **X**.

Compound **XVI** (lupan-20,28-diol-3-one) was purified further by preparative TLC using toluene/ethyl acetate (10:13) and recrystallized from 95% EtOH to give 11 mg of colorless needles, m.p. 231-232°. CI-HRMS $[M+1]^+$ 459.3825 calculated for $C_{30}H_{50}O_3$, found 459.3820. MS m/e (rel. int.) 440 (M^+-H_2O, 33), 425 (12.5), 409 (62), 369 (33), 286 (18), 245 (16), 234 (16), 219 (12), 203 (72), 189 (56), 175 (42), 163 (37), 149 (49), 135 (60), 119 (54), 107 (54), 95 (60), 81 (56), 59 (100). IR (NaCl) cm^{-1} 3390 (OH), 1700 (C=O), 1024 (C-O). ^{1}H-NMR ($CDCl_3$, J=Hz) δ: 0.94-1.24 (21H, s, 7 x Me), 2.43 (2H, m, H-2), 3.37 (1H, d, J=11, H-28), 3.84 (1H, d, J=11, H-28).

Compound **XVII** (lupan-3β-ol-29-oic acid) was purified by preparative TLC using toluene/ethyl acetate (5:3) to give 2 mg of colorless needles, m.p. 284-285°. MS m/e (rel. int.) 458 (M^+, 10), 440 (19), 425 (11), 385 (25), 367 (11), 289 (6), 235 (5), 221 (18), 207 (50), 189 (80), 175 (29), 163 (29), 147 (48), 135 (48), 121 (60), 107 (69), 95 (76), 81 (85), 67 (62), 55 (91), 43 (100). IR (NaCl) cm^{-1} 3380-2500 (OH, CO_2H), 1703 (C=O), 1128, 1068 (C-O). ^{1}H-NMR ($CDCl_3$, J=Hz) δ: 0.76-1.04 (18H, s, 6 x Me), 1.17 (3H, d, J=7.6), 2.80 (1H, d q, J=7.6, H-20), 3.19 (1H, m, H-3α). Acetylation of this compound with acetic anhydride/pyridine produced the monoacetate. MS m/e (rel. int.) 500 (M^+, 3), 440 (M-AcOH, 18). IR (NaCl) cm^{-1} 3300-2500, 1700 (CO_2H), 1735 (C-OAc), 1244, 1027 (C-O). ^{1}H-NMR ($CDCl_3$, J=Hz) δ: 0.74-1.04 (18H, s, 6 x Me), 1.17 (3H, d, J=7.6, H-30), 2.82 (1H, d q, J=7.6, H-20), 4.45 (1H, m, H-3α). This spectral data is in agreement with that in the literature [25].

SUMMARY AND CONCLUSIONS

Seventeen triterpenes, including four new compounds, were isolated and identified from the outer bark of yellow birch (*B. alleghaniensis*). The total content of triterpenoid components was 3.5% (based on dry bark), which is considerably higher than that observed previously in *B. lenta*, another dark-barked species. In general, the compounds in *B. alleghaniensis* were more highly oxidized than those in *B. lenta*. These differences may have taxonomic significance.

Although the overall content of triterpenes in yellow birch is not particularly high, there is potential for utilization of the bark for specialty chemicals because of widespread use of this species. The bark contains a diverse collection of triterpenes, some of which may have high biological activity. The products must have a high value, however, since chromatographic separation and purification is necessary.

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