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# Betulin isolation from birch bark by vacuum and atmospheric sublimation. A thermogravimetric study

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**Abstract**

Isolation of betulin from *Betula papyfera* bark can be performed both by chemical extraction or thermal sublimation. With the thermal sublimation method, no toxic nor expensive solvent is used. The scientific literature, however, reports very limited information about the sublimation method. In this work, a thermogravimetric study has been performed for the thermal sublimation of betulin from *B. papyfera* bark; the objective was to determine the optimum sublimation conditions. The study was carried out over a wide range of temperatures (30–550 °C) under two different pressures: atmospheric pressure and a pressure of 3.3 kPa. Under atmospheric pressure, the betulin sublimation takes place in the temperature range of 250–370 °C. Betulin evolves simultaneously with volatile materials evolving during the thermal decomposition of the bark. As a result, large amounts of impurities are found. Under a low pressure of 3.3 kPa absolute, the betulin sublimation temperature decreases by 50–70 °C. The betulin is, thus, more neatly separated from the bark thermal decomposition products. The remaining products can be separated from the betulin by choosing adequate condensation conditions.


*Keywords:* Betulin isolation; Birch bark; Sublimation; Thermogravimetry

## 1. Introduction

Interest in betulin has increased recently as certain derivatives from this compound are considered to be a potential agent against tumoral cancer [1–3] and HIV [4,5]. The molecular structure of betulin is given in Fig. 1. There are basically two approaches to isolate betulin from birch bark: chemical extraction [6,7] and sublimation [8]. The problem with the extraction method is that toxic, expensive solvents are used. Besides, limited purity is usually achieved due to the lack of selectivity of the solvents used.

Sublimation consists of the direct phase change of a compound from solid to gas [9]. The vapor product is recovered as a solid after a condensation stage without passing through the liquid phase. When applying sublimation to isolate betulin from birch bark, the bark must be heated to a certain temperature (close to the sublimation temperature of pure betulin) and the temperature is held for a certain period of time in order to fully release the betulin from the birch bark. Compared with the chemical extraction method, this thermal method seems to be simpler and cheaper. However, there is a lack of information

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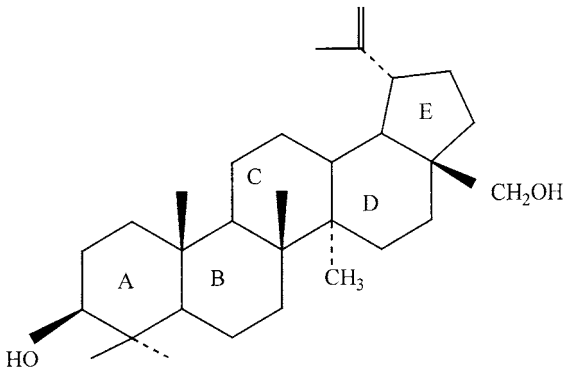


Fig. 1. Molecular structure of betulin.

on the thermal sublimation conditions from birch bark.

The objective of this work is to investigate betulin sublimation from birch bark under different temperature and pressure conditions, in order to determine the optimum sublimation conditions to obtain a high yield of good quality betulin.

Thermogravimetry (TG) is now a widely used method to study sublimation phenomena [10–12]. The advantage of the TG method is that it is fast and straightforward. In the TG furnace, the temperature and the pressure can be precisely controlled to reach the selected values. Using the TG method, only a small quantity of sample (<20 mg) is required. As a consequence, the influence of both the heat transfer and the mass transfer on the sublimation process can be ignored.

In the present work, a thermogravimetric analysis was used to study the sublimation of betulin from birch bark. The first objective of the study is to determine the sublimation temperature of the betulin in the birch bark, which is likely different from that of pure betulin. TG studies have been carried out on both the fresh bark which contains betulin and the extracted bark residue which is betulin-free. The difference between the DTG curves of fresh bark and the extracted bark residue can shed light on the sublimation behavior of betulin in birch bark. The second objective was to determine the optimum conditions at which the impurities can be segregated as much as possible. A series of isothermal TG tests on fresh bark have been carried out at different temperatures, which resulted in a group of samples labeled “thermal sublimation residue”. A TG study on these sublimation residues has been carried out. A comparison of the DTG curves of the sublimation residue and that of fresh bark revealed the betulin sublimation behavior under different sublimation conditions.

One should recall that the lower the pressure, the lower the sublimation temperature. This phenomenon can help separate the sublimated betulin from the bark decomposition products. In this work, the TG study on betulin sublimation has been carried out at two different pressure conditions with the objective to investigate the pressure influence on the betulin sublimation.

## 2. Experimental

### 2.1. Samples collection and preparation

The *Betula papyfera* bark was collected in the area of Gentilly, Québec, Canada, which included both phloem and rhytidome bark. Three types of birch bark samples have been prepared in this study [13]: the fresh bark, the solvent extracted bark residue and the isothermal sublimation bark residue. The fresh bark was air dried more than 100 h and then stored at ambient temperature in a plastic bag. The sample of solvent extracted bark residue was prepared by refluxing the fresh bark in methanol for 6 h. It was then air dried for more than 100 h and stored in a plastic bag. The sample of isothermal sublimation residue was prepared by putting the fresh bark in the furnace of TG instrument. Then the bark was heated isothermally at a pre-selected temperature for more than 1 h. The isothermal sublimation residue has a reduced betulin content.

In the literature, it is commonly accepted that the betulin content can be almost totally removed from birch bark by methanol extraction. Thus, the “Methanol Extraction Method” is often used to determine the betulin content in a specific birch bark species [7]. In this work, the extractives have been analyzed by GC/MS. The analysis indicated that the birch bark used for this study contains 6.7 wt.% of betulin.

### 2.2. Apparatus

The TG analysis was performed in a TGA/DTA 220 apparatus (Seiko Instruments) connected to a Seiko model 5200 station for data collection. Two different

pressures have been applied in the experiments: atmospheric and 3.3 kPa absolute. For the tests performed at atmospheric pressure, high purity $N_2$ gas at a flow rate of 150 ml/min was used as sweeping gas. For all of the tests, the initial sample mass was comprised between 3.8 and 4.9 mg.

### 2.3. Methodology

The present work can be divided in four major steps. In the first step, a dynamic TG study of fresh bark was undertaken to understand the weight loss behavior of all materials comprising the birch bark, including the betulin sublimation, the evolution of low volatile matters and the bark decomposition. The second step of this study consisted of performing a dynamic TG study of the extracted bark residue sample. It is believed that the extracted bark residue sample is betulin-free [7]. Then a comparison of the DTG curve of the extracted residue sample and that of fresh bark was carried out to isolate the behavior of betulin sublimation from birch bark. In the third step, isothermal sublimation has been studied at different heating temperatures which are in the range of the betulin sublimation temperature determined under dynamic heating. Then, a series of isothermal dynamic TG tests has been carried out to study the residues (called isothermal sublimation residue samples) produced from the isothermal tests. Finally, a comparison of the DTG curves of the isothermal sublimation residue and that of fresh bark was performed. The differences between the two groups of DTG curves have been used to determine the amount of betulin and impurities released during the isothermal tests.

In the dynamic heating tests, the sample was heated from 30 to 550 °C at a heating rate of 10 °C/min. In the isothermal tests, the sample was heated from 30 °C to the final selected temperature at a heating rate of 10 °C/min; the selected temperature was then held constant for 1 h.

All the tests were performed at two different pressures: atmospheric and a low pressure (3.3 kPa absolute) with the objective to study the influence of pressure on the mechanism of betulin sublimation.

## 3. Results and discussion

### 3.1. Sublimation of betulin from birch bark under atmospheric pressure

#### 3.1.1. TG study on the fresh birch bark

Fig. 2 shows the TG and the DTG curves of birch bark obtained under atmospheric pressure. The TG

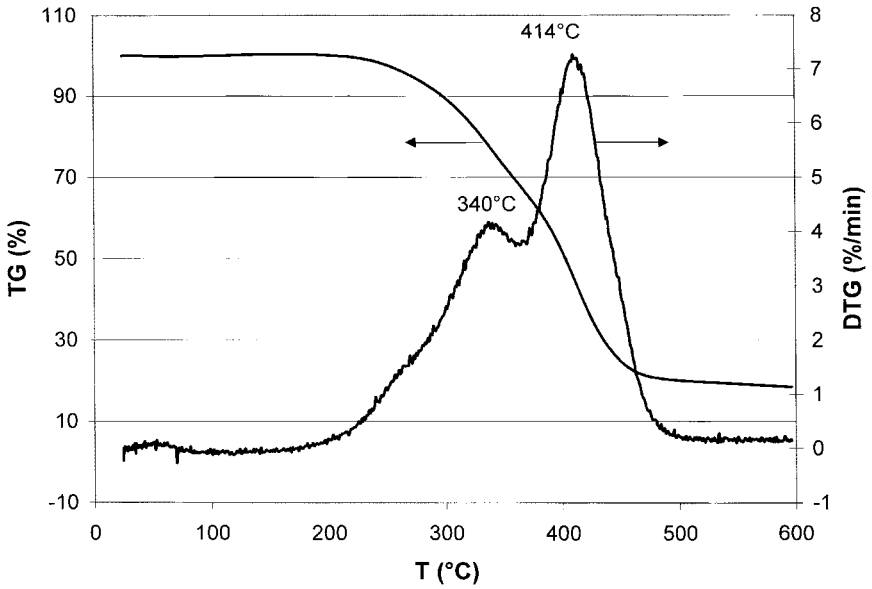


Fig. 2. TG and DTG curves of birch bark obtained under atmospheric pressure.

curve shows a total weight loss of 81.5% in the temperature range of 30 to 600 °C. The DTG curve is characterized by two peaks. The first peak can be identified in the temperature range of 170–370 °C, with a peak at 340 °C. The second peak is found in the temperature range of 370–500 °C, at 414 °C. Several authors have indicated that during the heating of lignocellulosic materials, basically two types of phenomena occur: the evolution of low volatile matters takes place in the temperature range of 50–275 °C while the thermal decomposition of the lignocellulosic material occurs in the temperature range of 200–500 °C [14,15]. When reviewing the DTG curve in Fig. 2, it could then be concluded that the first peak mainly corresponds to the evolution of the low volatile matters. The second peak is the trace left by the decomposing lignocellulosic material.

A preliminary investigation of the authors [13] did indicate that pure betulin sublimates in the temperature range of 200–370 °C. Assuming the betulin in the birch bark has a similar sublimation temperature as that of pure betulin, the betulin sublimation phenomenon should occur in the area of the first peak and thus, overlaps with the evolution of low volatile matters and the bark pyrolysis phenomena.

The overlap of betulin sublimation with the volatilization and the thermal decomposition of bark influences the betulin sublimation in three aspects. First, the sublimation temperature of betulin may not be the same as that of pure betulin due to the physical and/or chemical interactions between betulin and the other compounds. Second, the overlap of the sublimating betulin phenomenon with the release of other compounds makes it difficult to detect the individual behavior of betulin sublimation as a function of temperature. Thirdly, the simultaneous release of the products from the volatilization step and the thermal decomposition of bark introduces impurities to the betulin fraction.

### *3.1.2. TG study on the extracted bark residue sample*

In order to better understand the single behavior of betulin sublimation from birch bark, the extracted birch bark residue which is betulin-free, has been studied by TG and then compared with TG data involving fresh bark which contains 6.7% betulin.

The curve a in Fig. 3 illustrates the DTG curve of the extracted birch bark residue. It shows a single peak at 413 °C with a shoulder located at about 260 °C. Comparing the DTG curve of fresh bark (curve b in Fig. 3), a significant difference can be observed in the temperature range of 250–372 °C for the first peak. It simultaneously shows, however, a quasi perfect overlap of the two curves in the following temperature ranges: 30–260 and 372–550 °C. Recalling that the difference between the two samples is that the

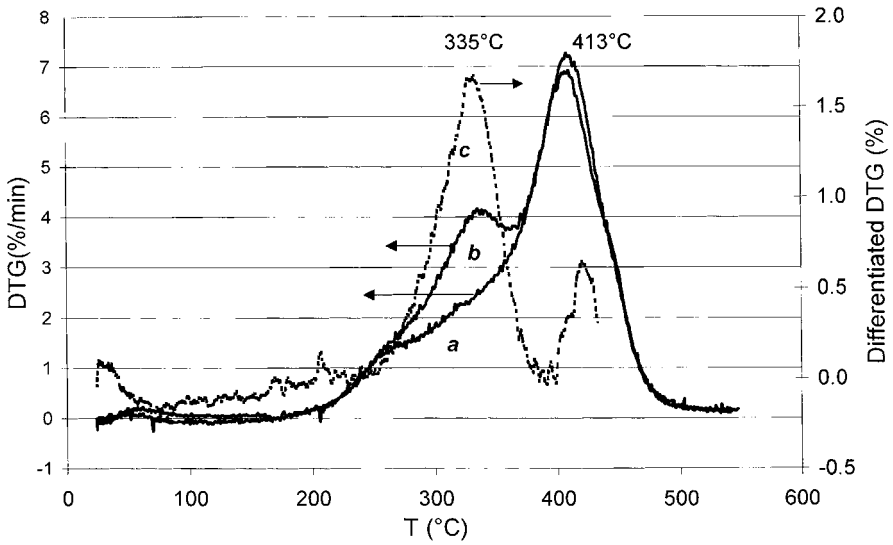


Fig. 3. DTG curves of (a) extracted bark residue sample, (b) fresh bark and (c) the difference between curves a and b.

extracted residue sample has been pre-treated by solvent extraction, the difference between the two DTG curves actually represents the DTG behavior of the material, which has been isolated by solvent extraction.

Curve c in Fig. 3 shows the difference between the DTG curve of the extracted residue and that of the fresh bark. It is obtained by subtracting curve a from b in Fig. 3. On curve c, a major peak is observed in the temperature range of 250–372 °C. The maximum DTG value is reached at 335 °C. Differences between the two DTG curves below 250 °C and after 372 °C are believed to be associated with experimental limits of the method. The area under curve c in the temperature range of 250–372 °C has been calculated to be equal to 9.6%, representing the difference in weight losses between the fresh bark and the extracted residue samples. Since this weight loss difference is caused by the extracted residue sample having a pre-weight loss during the solvent extraction treatment, the 9.6% weight loss under curve c actually represents the weight loss during the solvent extraction of birch bark. Since there is 6.7% betulin obtained from solvent extraction, the amount of other compounds involved in curve c can, thus, be estimated at 2.9%. This result implies that betulin sublimation is the dominating phenomenon involved in curve c. Curve c in Fig. 3 can, thus, be considered to quite well represent the behavior of betulin sublimation under atmospheric pressure.

Our previous TG study on pure betulin showed that pure betulin sublimation occurred in the temperature range of 200–370 °C, and reached the maximum sublimation rate at 364 °C [13]. The above study shows that the betulin sublimation from birch bark seems to start at a higher temperature and end at a lower temperature compared with pure betulin. This phenomenon is believed to be caused by the interaction between betulin and the other compounds contained in the birch bark. Consequently, when applying the thermal sublimation technique to isolate betulin from birch bark, the data from the pure betulin sublimation study cannot be directly used. The behavior of betulin sublimation from birch bark should, therefore, be studied independently.

### *3.1.3. TG study of betulin sublimation under isothermal condition*

A sublimation process is traditionally carried out at an isothermal condition. The purpose of holding the temperature at a certain value is to restrain the release of other compounds during sublimation and thus to lower the amount of impurities collected. The TG study under dynamic heating conditions (see curve c in Fig. 3) indicates that the betulin sublimation from birch bark covers a wide temperature range from 250 to 372 °C. In this temperature range, however, impurities of both the low volatile matters and the bark decomposition products are unavoidably generated. The objective of isothermal sublimation is to find the optimum sublimation conditions at which a high yield of betulin as pure as possible can be achieved.

Fig. 4 illustrates seven isothermal TG curves of fresh birch bark samples carried out at temperatures comprised between 193 and 256 °C (10 °C increments between each trial) under atmospheric conditions. As one might expected, the higher the temperature, the higher the weight loss. Table 1 presents the weight loss during each one of the isothermal tests. The table reveals that for the tests at a temperature less than or equal to 214 °C, the total weight loss during a test is always less than 3.8%. Since birch bark contains 6.7% of betulin, heating birch bark at a temperature lower than 214 °C cannot isolate all of the betulin contained in the bark. As for the test at 256 °C, the weight loss reaches 19.8%, a value much higher than the betulin content in the bark. Thus, a large amount of impurities are involved during the betulin evolution under atmospheric pressure conditions.

### *3.1.4. TG study on the isothermal sublimation residue samples*

Isothermal TG study can indicate the amount of weight loss under different heating temperatures. The weight loss data, however, is not sufficient to determine which compounds have been released during the test. Hence, the residues from the isothermal TG tests (called the isothermal sublimation residue samples) were re-evaluated by TG and the resulting DTG curves were compared with the DTG curves of fresh bark. The difference between the two curves can help detect the amount of betulin and impurities released during the isothermal tests.

Fig. 5 illustrates the DTG curves of the sublimation residue samples (curves b–e) in comparison with the DTG curve of fresh bark (curve a). The figure shows a significant difference between the DTG curves in the temperature range of 170–370 °C, the temperature

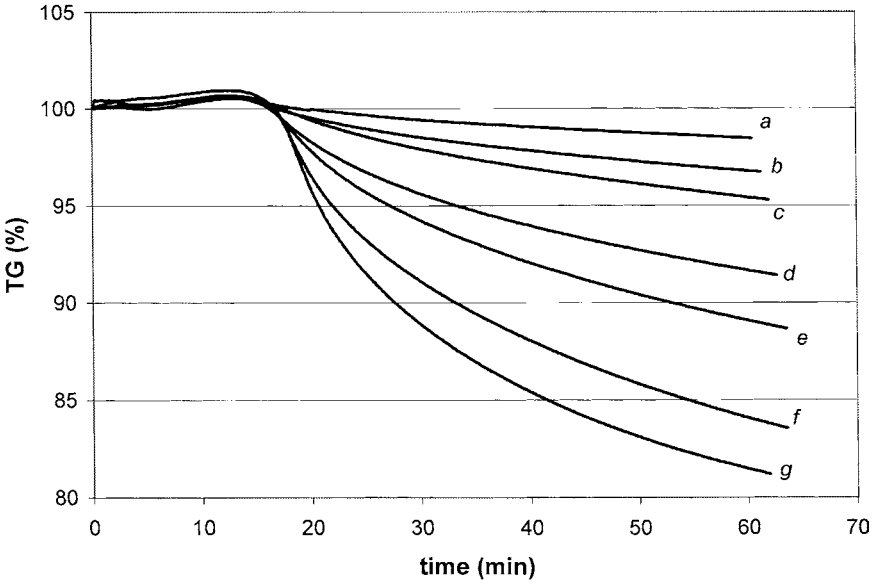


Fig. 4. TG curves obtained under isothermal conditions, at temperatures of (a) 193 °C, (b) 203 °C, (c) 214 °C, (d) 225 °C, (e) 235 °C, (f) 246 °C and (g) 256 °C.

range in which the first peak of the DTG curve of fresh bark is located. The DTG curve of fresh bark (curve a) with a full first peak can be well observed. The DTG curves of the sublimation residue samples have a reduced first peak. The degree to which the first peak is reduced increases with the temperature at which the sublimation residue sample was produced. In the case of the DTG curve of the residue sample at 256 °C (curve e), virtually no peak is observed for that specific temperature range. Knowing that the betulin sublimation is comprised within the first peak, the shrink of the first peak with the increasing heating temperature indicates that: (1) isothermal heating in the temperature range of 193–256 °C enables betulin to be released from birch bark; (2) the higher the heating temperature, the larger the yield of betulin; (3) an isothermal heating at a temperature of 256 °C or higher enables all the betulin to be released.

Table 1
Weight loss measured during the isothermal tests under atmospheric pressure

| Temperature (°C) | Weight loss (%) |
|---|---|
| 193 | 2.0 |
| 203 | 3.8 |
| 214 | 5.23 |
| 225 | 9.11 |
| 235 | 11.8 |
| 246 | 18.7 |
| 256 | 19.8 |

If curve a is considered as the baseline for zero betulin sublimation, the difference between curve a and the other curves in Fig. 5 actually indicates the amount of betulin that can be further obtained at a certain production temperature during the isothermal tests. Fig. 6 illustrates the differentiated DTG curves resulting from the subtraction of the DTG curve of the sublimation residue sample from that of fresh bark. For the curves at 193, 214, and 235 °C (curves a, b and c), two peaks are observed: a large one at 256 °C and a smaller one at 339 °C. In order to determine which of these peaks can be associated to the betulin sublimation, the DTG curve of betulin sublimation (curve c in Fig. 3) has been reproduced as curve e in Fig. 6. Due to the similar location of the peak of curve e and the peaks at the higher temperature (339 °C) on curves a, b, and c, it is believed that the peak at 339 °C is responsible for the betulin sublimation and the peak at the lower

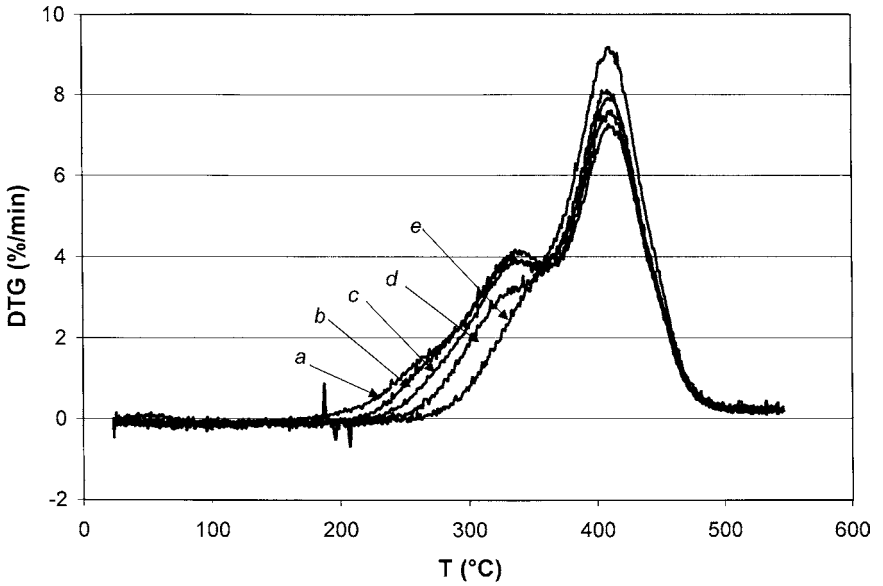


Fig. 5. DTG curves of the sublimation residue samples in comparison with the DTG curve of fresh bark (a). The sublimation residue samples were obtained at (b) 193 °C, (c) 214 °C, (d) 235 °C and (e) 256 °C.

temperature (256 °C) is, thus, associated with the impurities. To estimate the amount of impurities and the betulin released during the isothermal tests, Table 2 provides the area fraction under each peak for all the curves shown in Fig. 6. The data listed in column two of Table 2 represents the total weight loss in the temperature range of 170–370 °C. The third column was obtained after subtracting each data in column two

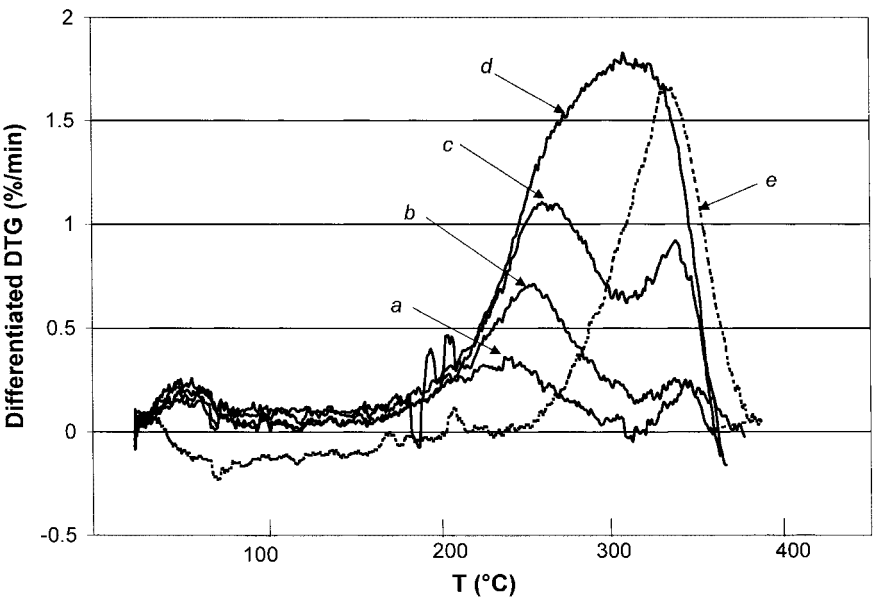


Fig. 6. The differentiated DTG curves obtained at (a) 193 °C, (b) 214 °C, (c) 235 °C and (d) 256 °C in comparison with the DTG curve of betulin sublimation (e).

Table 2
Weight loss of the fresh bark and the sublimated residue samples, in temperature range of 170–370 °C

| Samples | Total weight loss (%) | Incremental difference with fresh bark (wt.%) | Fraction of total area (%) | |
|---|---|---|---|---|
| | | | Under first peak | Under second peak |
| Fresh bark | 34.7 | 0 | 0 | 0 |
| Residue sample resulted at 193 °C | 31.3 | 3.4 | 79 | 21 |
| Residue sample resulted at 203 °C | 30.8 | 3.9 | 77 | 23 |
| Residue sample resulted at 214 °C | 29.4 | 5.3 | 87 | 13 |
| Residue sample resulted at 225 °C | 28.1 | 6.6 | 86 | 14 |
| Residue sample resulted at 235 °C | 22.6 | 12.1 | 74 | 26 |
| Residue sample resulted at 256 °C | 17.7 | 17.0 | – | – |

from the total weight loss of the fresh bark (34.7%), which represents the area under each curve (curves a–d) shown in Fig. 6. The data listed in columns four and five represent the fraction of impurities and the fraction of betulin displayed in Fig. 6, respectively. Table 2 shows a much higher fraction of impurities than that of betulin. From Table 2, the amount of betulin released at temperatures lower than 235 °C, is estimated to be less than 3.1% (12.1% × 26%). This amount is much less than the betulin contained in the birch bark (6.7%).

Unlike the other differentiated DTG curves a–c in Fig. 6, the differentiated DTG curve d at 256 °C exhibits only one peak. This peak is believed to be caused by the intensive release of both the impurities and the betulin during the test. In Table 2, the total weight loss associated with curve d is 17.0%. Assuming that all of the betulin content (6.7%) has been released during the isothermal test at 256 °C, the amount of impurities can thus be estimated to be 10.3%.

### *3.2. Sublimation of betulin from birch bark under a low pressure of 3.3 kPa*

The TG study under atmospheric pressure shows that the impurities produced together with betulin sublimation is the main problem associated with using a sublimation method to isolate betulin from birch bark. To lower the amount of impurities, sublimation at low pressure has been studied.

#### *3.2.1. TG study on fresh birch bark*

Fig. 7 illustrates the TG and the DTG curves of birch bark obtained under an absolute pressure of 3.3 kPa. The TG curve reveals a weight loss of 85% during heating. The DTG curve shows two independent peaks, located at 262 °C and at 405 °C. The previous study on pure betulin had shown that under 3.3 kPa, betulin sublimates in the temperature range of 220–300 °C. Assuming that betulin in birch bark has a similar sublimation temperature as pure betulin, the betulin sublimation should occur in the area of the first peak.

In comparison with the DTG curve measured under atmospheric pressure (see Fig. 2), one can observe that the first peak of the DTG curve under low pressure, appears at a lower temperature (about 80 °C lower). The second peak keeps almost the same shape as that measured at atmospheric pressure and shifts slightly (9 °C) downward. This result confirms that under lower pressure, the betulin sublimation and the evolution of the low volatile matters are taking place at a lower temperature. The thermal decomposition of bark almost follows the same behavior as that at atmospheric pressure. Thus, sublimation under a low pressure may enable the separation of the betulin from the impurities originating from bark decomposition.

#### *3.2.2. TG study on the extracted bark residue sample*

Under low pressure, betulin sublimates together with the low volatile matters. In order to detect the individual behavior of betulin sublimation from birch bark, the extracted bark residue sample has been studied by TG. The resulting DTG curves were then compared with the DTG curves of fresh bark. The difference between the two hypothetically represents the betulin sublimation behavior.

The DTG curve of the extracted birch bark is presented (curve a) and compared with that of the fresh bark (curve b) in Fig. 8. An obvious difference is

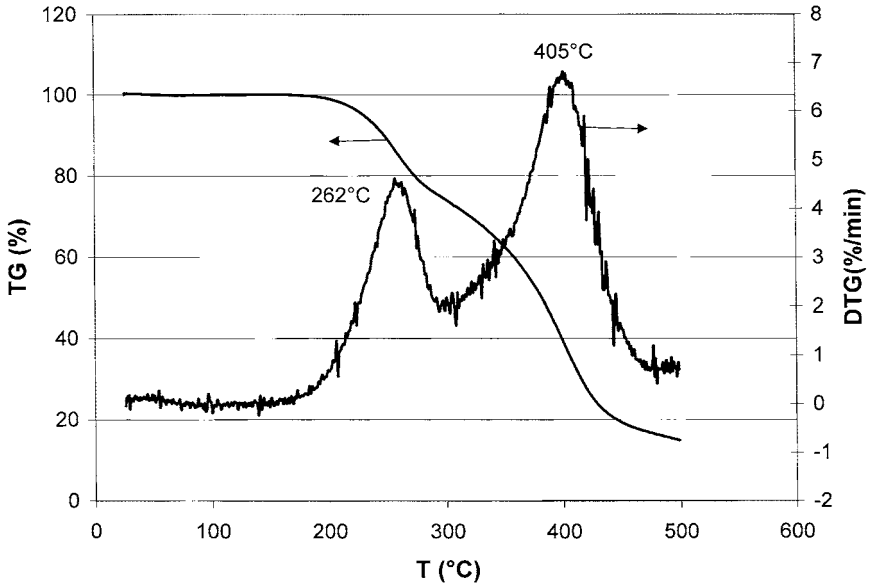


Fig. 7. TG and DTG curves of birch bark obtained under an absolute pressure of 3.3 kPa.

observed in the temperature range of 150–300 °C, where both betulin sublimation as well as the evolution of low volatile matters takes place. While curve b has a full peak, curve a exhibits only a small shoulder in the temperature range of 150–300 °C. Such a difference is due to an early weight loss of the extracted sample during the solvent extraction. In the temperature range of 300–450 °C, the two curves overlap, showing

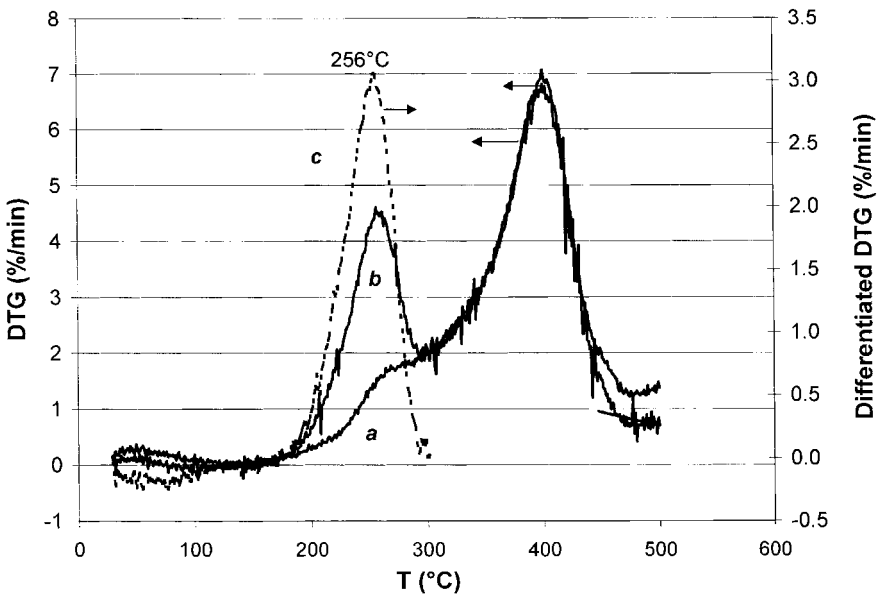


Fig. 8. DTG curves of (a) extracted bark residue sample, (b) fresh bark and (c) the difference between curves a and b, measured under pressure of 3.3 kPa.

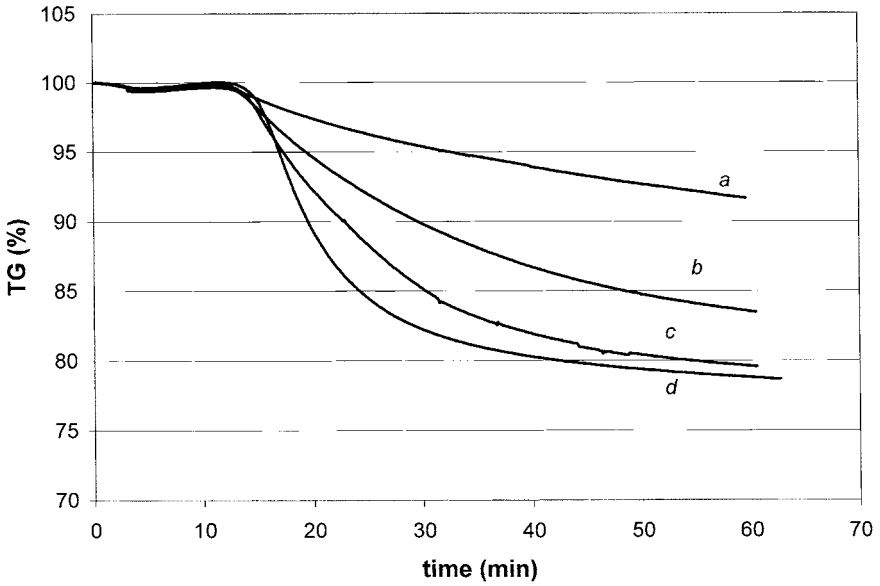


Fig. 9. TG curves obtained under isothermal vacuum conditions, at temperatures of (a) 193 °C, (b) 204 °C, (c) 212 °C and (d) 232 °C.

the same thermal decomposition behavior for the two samples. This agreement proves that the solvent treatment did not change the property of the bark decomposition process.

Subtracting the DTG curve of the extracted residue from that of fresh bark provides curve c in Fig. 8. This also demonstrates the betulin sublimation behavior under low pressure. A single peak is observed in the temperature range of 160–300 °C and the maximum DTG value is reached at 256 °C. This temperature is almost 40 °C lower than the sublimation temperature of pure betulin (294 °C) under the same pressure. Such a decrease of peak temperature is believed to be caused by the influence of the simultaneous evolution of other compounds during the betulin sublimation.

When comparing curve c in Fig. 8 with curve c in Fig. 3, the shapes of the two curves look very similar. The difference between the two curves is that curve c in Fig. 8 shifts downwards by about 80 °C, indicating the significant influence of pressure during betulin sublimation.

### *3.2.3. TG study on betulin sublimation under isothermal condition*

In order to achieve the maximum yield of betulin and to restrain the evolution of impurities, the isothermal sublimation under low pressure condition has been studied. Fig. 9 illustrates the TG curves of four isothermal tests carried out at four different temperatures (190, 200, 210 and 230 °C). The weight losses during each test are reported in Table 3. The same phenomenon as the one occurring at atmospheric pressure has been observed: as the heating temperature increases, the weight loss increases. Table 3 shows that for the tests carried out at a temperature of 190–230 °C, the total weight loss during the tests is 8.4–21.4%. These weight losses are much higher than the weight loss observed at the same heating temperature under atmospheric pressure.

### *3.2.4. TG study on the isothermal sublimation residue samples*

In order to determine which compounds have been released during the isothermal tests under low

Table 3
Weight loss during isothermal heating under 3.3 kPa absolute

| Temperature (°C) | Weight loss (%) |
|---|---|
| 193 | 8.4 |
| 204 | 16.5 |
| 212 | 20.5 |
| 232 | 21.4 |

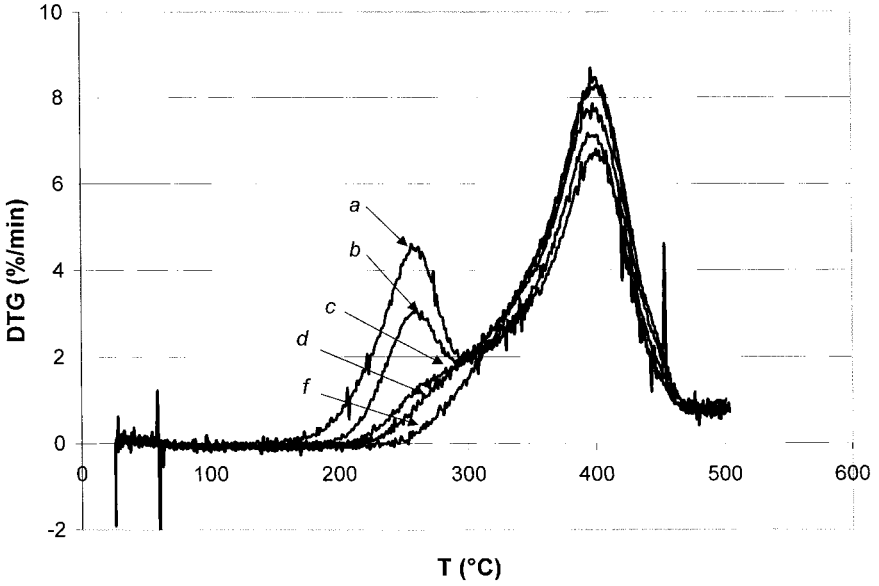


Fig. 10. DTG curves of the sublimation residue samples in comparison with the DTG curve of fresh bark (a). The sublimation residue samples were obtained at (b) 193 °C, (c) 204 °C, (d) 212 °C and (e) 232 °C under pressure of 3.3 kPa.

pressure, the isothermal sublimation residue samples were again subjected to TG determination at low pressure. The resulting DTG curves were then compared with the DTG curve of fresh bark.

Fig. 10 illustrates the DTG curves of the sublimation residue samples (curves b–d) compared with the DTG curve of fresh bark (curve a). This Figure shows a significant difference between the DTG curves in the first peak and an overlap for all the second peaks. This result indicates that the first peak represents the compounds released during the isothermal tests. From Fig. 10, the fullness of the first peak decreases with the heating temperature associated with the isothermal tests during which the sublimation residue samples were produced. Once the temperature reaches 230 °C, the first peak on the DTG curve of the sublimation residue sample almost disappears. Since the first peak is associated with the betulin sublimation and the evolution of low volatile matters, the variation of the first peaks in Fig. 10 indicates that: (1) isothermal heating in the temperature range of 190–230 °C enables the betulin content to be released from the birch bark, together with the evolution of some low volatile matters; (2) the higher the heating temperature, the larger the yield of betulin; (3) once the heating temperature has reached 230 °C, almost all of the betulin content has been released.

Considering curve a as the baseline for zero betulin sublimation, the difference between curve a and the other curves in Fig. 10 has been calculated and used in Fig. 11 to illustrate the increase of betulin production with the heating temperature of the isothermal tests. The differentiated DTG curves in Fig. 11 are obtained by subtracting the DTG curves of sublimation residue samples from that of fresh bark. Only one peak is observed on each of the curves in Fig. 11. This peak is located at 170–300 °C, and has its maximum at 258 °C. When comparing the betulin sublimation behavior obtained from the study of extracted residue (curve e), all the curves in Fig. 11 have a shape and location which is similar to that of curve e. It is, thus, believed that the product from isothermal heating under low pressure is composed of compounds which are similar to those isolated from birch bark which has been subjected to solvent extraction. Knowing that the compounds from solvent extraction are betulin dominated, it can thus be concluded that the products from isothermal sublimation under low pressure contain a high fraction of betulin.

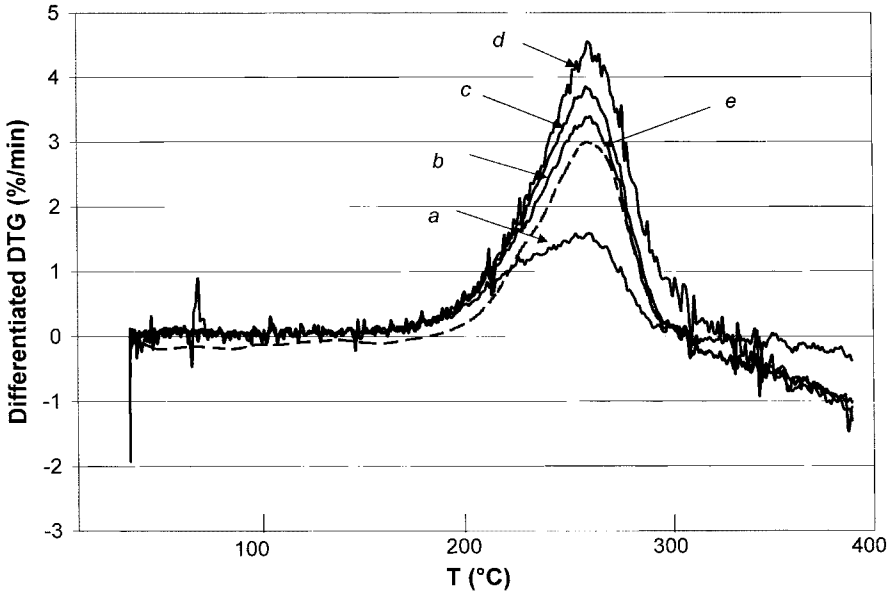


Fig. 11. The differentiated DTG curves obtained at (a) 193 °C, (b) 204 °C, (c) 212 °C and (d) 232 °C in comparison with the DTG curve (e) of betulin sublimation.

In Fig. 11, curve a has a smaller peak than in curve e, indicating that an isothermal heating at 193 °C is not able to completely isolate the betulin content in birch bark. Curves b–d have larger peaks than curve e, indicating that the isothermal heating of birch bark at a temperature ≥204 °C produces more impurities than solvent extraction of birch bark. Curve b in Fig. 11 is very close to curve e. It can, thus, be assumed that an isothermal heating at 204 °C might be the best condition to sublimate betulin from birch bark, under a total pressure of 3.3 kPa.

Table 3 shows the weight losses involved in curves b–d, which are 16.5–21.4%. Assuming that all of the betulin (6.7%) has been released during the isothermal test of b–d, the amount of impurities released together with betulin sublimation can be estimated to be 9.8–14.7%. This means a concentration of impurities of approximately 60–70%. Compared with the betulin yield of sublimation obtained under atmospheric pressure, the sublimation yield obtained under a low pressure generates a much lower amount of impurities. A more important difference between the two is that the impurities from low pressure sublimation contain no bark decomposition products which are heavier and difficult to separate. This will facilitate the subsequent purification of the betulin obtained.

A well intended condensation method is often applied as an effective means to segregate the impurities by controlling the condensation temperature at a narrow and appropriate range. For example, the low volatile matters from birch bark have a lower condensation temperature than that of betulin. Thus, choosing a condensation temperature higher than that of these low volatiles might effectively segregate the low volatiles. This method will not, however, be able to segregate decomposition-derived impurities which have a lower condensation temperature than betulin. As thermal decomposition under low pressure can successfully segregate the impurities from bark decomposition, using low pressure sublimation plus a well designed desublimation process should lead to the production and recovery of high quality betulin. This is an on going project in our laboratories.

## 4. Conclusions

External bark of *Betula verrucosa* in Europa and *B. papyfera* in North America is recognized for its high

content in betulin. This betulin can be isolated using chemical or thermal techniques. Compared with the chemical extraction method, the thermal sublimation method is simple and does not require expensive nor toxic solvents. This study has brought new information about betulin sublimation from birch bark, such as the optimal sublimation temperature and pressure, the yield of betulin under different heating conditions and the fraction of impurities contained in the betulin obtained. This information is essential prior to applying a sublimation process to isolate betulin from birch bark. A careful study of fresh bark, solvent extracted residue and isothermal sublimation residue samples by means of TG has led to the following major conclusions:

(1) Under atmospheric pressure, betulin sublimating from birch bark overlaps with the low volatile matter and bark decomposition products. As a result, the betulin sublimation process follows a different mechanism as compared to pure betulin. Second, the simultaneous release of the products from the volatilization and the thermal decomposition of bark results in impurities in the betulin product.
(2) Under dynamic heating conditions, betulin sublimation from birch bark under one atmosphere starts at 250 °C, reaches a maximum at 335 °C and ends at 372 °C.
(3) Isothermal heating at 260 °C under one atmosphere enables the sublimation of most of the betulin contained in the birch bark. The betulin obtained contains, however, about 74–87% of impurities which consist of some low volatile matters and bark decomposition products.
(4) At low pressure (3.3 kPa absolute), the sublimation temperature of betulin and the temperature at which the low volatile matters evolve is much lower than that at atmospheric pressure. The bark decomposition phenomena take place at almost the same temperature as that measured at atmospheric pressure. As a result, sublimation under low pressure enables the impurities to be segregated from the by-products of the bark thermal decomposition process, thus lowering and simplifying the amount and composition of the impurities.
(5) At 3.3 kPa, the betulin sublimation from birch bark starts at 160 °C, reaches a maximum at 256 °C and ends at 300 °C, under dynamic heating conditions. These temperatures are about 80 °C lower than those measured under atmospheric pressure.
(6) At 3.3 kPa, an isothermal heating at 200 °C is believed to represent the best conditions to sublimate betulin from birch bark. Such conditions enable the sublimation of most of the betulin contained in the birch bark. Between 60 and 70% of impurities are found, which basically consist of low volatile materials.

Compared with atmospheric pressure conditions, the betulin sublimation at 3.3 kPa takes place at a lower temperature and produces less impurities. The more important difference between the two approaches is that the impurities from low pressure sublimation contain no bark decomposition products, making it easier for the subsequent purification of the sublimation products.

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