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THERMAL BEHAVIOUR OF SOME TERPENOIDS

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Abstract

The terpenoids acetyl sitosterol, lupeol, acetyl diosgenin and stigmasterol were studied. Comparison of the thermogravimetric curves and the activation energies of the terpenoids suggested the following sequence of thermal stability: acetyl sitosterol < acetyl diosgenin < lupeol < stigmasterol. The DSC curves allowed determination of the melting points and the degrees of purity. Comparison of the TG and DSC curves revealed the presence of phase transitions without mass loss that were attributed to rearrangements in the terpenoid molecules.

Keywords: DSC, terpenoids, TG, thermal behaviour

Introduction

There is growing interest in the thermal properties of substances in different technological areas, and especially thermal techniques (TG and DSC) are becoming powerful analytical instruments for characterization of such compounds.

Studies of the thermal behaviour of medicinal plant substances by means of thermal techniques are rather rare in the literature. The objective of the present work was to analyse the thermal behaviour of some natural terpenoids by TG and DSC.

Experimental

Chemicals

All of the studied compounds were obtained from natural sources: lupeol from Bowdichia virgilioides [1], and sitosterol, stigmasterol and diosgenin from Dioscorea cayenensis var. rotundata [2]. They were identified through ^{1}H and ^{13}C NMR spectroscopy. The compounds acetyl diosgenin and acetyl sitosterol were prepared by acetylation (Ac_2O/py, reflux, 2 h). These substances have been deposited in the Bank of Standards of Natural Products of the Laboratório de Tecnologia Farmacêutica of the Universidade Federal da Paraíba. Before use in this work, they were repurified: lupeol and stigmasterol by TLC, using the hexane:chloroform (8:2)

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system, and acetyl diosgenin and acetyl sitosterol by recrystallization from ketone and benzene, respectively.

Methods

The TG curves were obtained in a Shimadzu TGA-50 thermobalance, using an alumina pan and a heating rate of 10°C min^{-1}, in the temperature range 25–900°C, in an atmosphere of air flowing at 20 ml min^{-1}. The amount of the sample was 10 mg. The DSC curves were obtained with a Shimadzu DSC-50 differential scanning calorimeter in the temperature range 25–500°C, using an aluminium pan, at a heating rate of 10°C min^{-1}. A nitrogen atmosphere was used, at a flow rate of 50 ml min^{-1}. The TG and DSC curves were analysed with the aid of the software TASYS from Shimadzu. The DSC temperature scale was calibrated with the USP phenacetin melting point reference standard.

The activation energy was obtained by the methods of Ozawa (OZ) [3], Coats and Redfern (CR) [4], Madhusudanan *et al.* (MD) [5], Horowitz and Metzger (HM) [6] and Van Krevelen *et al.* (VK) [7].

Results and discussion

Lupeol exhibits one decomposition stage in the temperature range 303–534°C, with a mass loss of 99.3%. Acetyl diosgenin undergoes thermal decomposition in four steps, in the temperature ranges 290–334, 334–385, 395–494 and 494–553°C, with mass losses of 25.7, 54.0, 12.1 and 7.0%, respectively. The thermal decomposition of acetyl sitosterol occurs in three stages, in the temperature ranges 271–312, 312–350 and 350–604°C, with mass losses of 38.2, 49.9 and 10.7%. Stigmasterol takes part in thermal decomposition in four steps, in the temperature ranges 294–335, 335–374, 374–501 and 501–605°C, with mass losses of 33.8, 46.0, 11.4 and 8.7%, respectively. The thermogravimetric data allowed calculation of the E_a values (activation energies) of the substances by the five methods:

lupeol – OZ (97.9), CR (96.0), MD (99.5), HM (117.1) and VK (105.9 kJ mol^{-1});

acetyl diosgenin – OZ (96.8), CR (87.3), MD (87.7), HM (107.4) and VK (97.2 kJ mol^{-1});

acetyl sitosterol – OZ (84.9), CR (88.8), MD (85.6), HM (106.8) and VK (97.8 kJ mol^{-1});

stigmasterol – OZ (102.9), CR (96.4), MD (97.6), HM (114.9) and VK (107.8 kJ mol^{-1}).

For the integral OZ, CR and MD methods, the mean values of the activation energies of the substances were: lupeol: 97.8±1.8, acetyl sitosterol: 86.4±2.1, acetyl diosgenin: 90.6±5.4 and stigmasterol: 99.0±3.5 kJ mol^{-1}. The dispersion in the data obtained by these methods is lower than that in the mean values obtained by the HM and VK methods: lupeol: 111.5±7.9, acetyl sitosterol: 102.3±6.4, acetyl diosgenin: 102.3±7.2 and stigmasterol: 111.4±5.0 kJ mol^{-1}. This suggests the use of the integral methods to obtain the activation energies of the substances studied in the present work.

The thermogravimetric data on lupeol, acetyl diosgenin, acetyl sitosterol and stigmasterol reveal that the substances exhibit different thermal behaviour. Acetyl sitosterol requires a lower temperature for decomposition than the other terpenoids, as confirmed by the kinetic data, the activation energies of the terpenoid compounds suggesting the following sequence of stability: acetyl sitosterol < acetyl diosgenin < lupeol < stigmasterol.

The DSC curves allowed calculation of the temperatures of the phase transition, the melting points and the degrees of purity of the substances (Table 1). The DSC temperature scale was calibrated with USP phenacetin melting point reference standard 99.9% purity, *m.p.* (135°C) [8]. The melting point values obtained from the DSC curves for lupeol (216°C) and acetyl sitosterol (129°C) were similar to those in the literature [8].

Table 1 Calorimetric behaviour of some natural terpenoids

Substance	Melting point/°C	Degree of purity/%
Lupeol	215.9	93.8
Acetyl diosgenin	193.1	92.8
Acetyl sitosterol	129.2	96.1
Stigmasterol	159.9	91.1

Acetyl diosgenin (193°C) and stigmasterol (159°C) gave phase transition peaks that were quite different from those in the literature [8]. The differences between the melting points obtained by DSC and those in the literature may be related with the impurities in the acetyl diosgenin and stigmasterol. Lupeol and acetyl sitosterol contained impurities which caused less interferences. Table 1 demonstrates that the products had degrees of purity above 90%.

The DSC curve (Fig. 1) of lupeol reveals the presence of five phase transitions, without mass loss in the TG curve. The first four peaks are attributed to molecular rearrangements occurring in the chiral centres of the molecule, and fifth relating to the melting of the substance.

For acetyl diosgenin (Fig. 2), the DSC curve presents two phase transitions, without mass loss in the TG curve. The first is attributed to molecular rearrangement and the second to the melting of the substance.

The TG and DSC curves of acetyl sitosterol (Fig. 3) show that the first peak of phase transition without mass loss is related to a molecular rearrangement. The second peak, at 290°C, is characteristic of the melting process.

Stigmasterol (Fig. 4) displays the presence of three thermal processes in the DSC curve. The first corresponds to molecular rearrangement without mass loss. The second without mass loss is attributed to the melting of stigmasterol.

Analysis of the TG and DSC data on lupeol, acetyl diosgenin, acetyl sitosterol and stigmasterol allow the suggestion that the thermal characterization is fundamental for optimization of the extraction methodologies and natural drug purification so

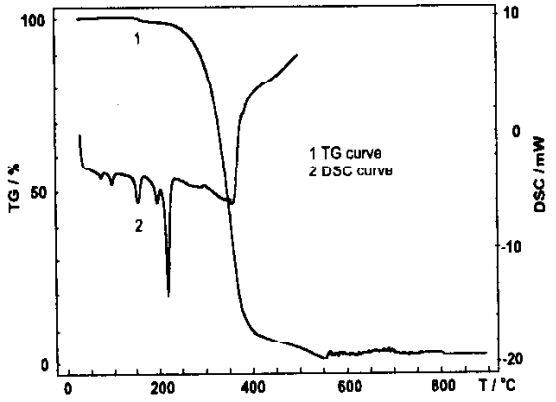

Fig. 1 TG and DSC curves of lupeol

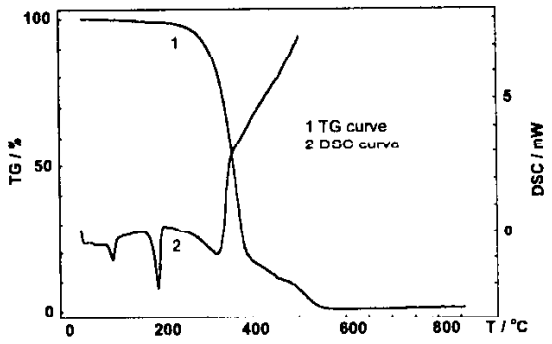

Fig. 2 TG and DSC curves of acetyl diosgenin

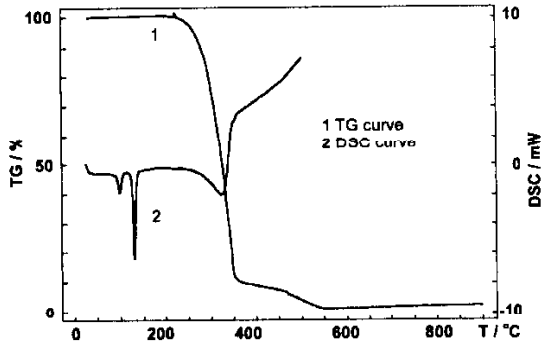

Fig. 3 TG and DSC curves of acetyl sitosterol

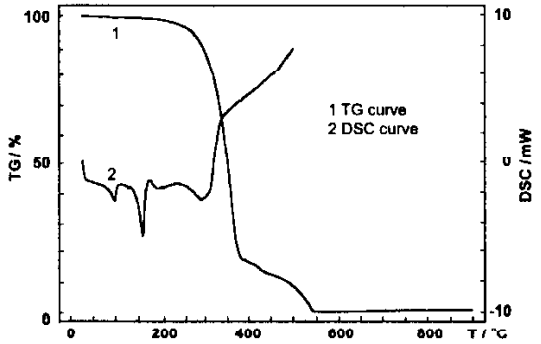

Fig. 4 TG and DSC curves of stigmasterol

as to guarantee presentation of the biological/pharmacological activity in the bioactive natural products.

Conclusions

The melting points and degrees of purity of the natural terpenoids were determined by DSC, in a simple, rapid and precise method.

The presence of phase transitions in the DSC curves without mass losses in the TG curves indicates the need for studies on the chemical structure *vs.* the biological activity in these natural terpenoids.

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References

1 L. C. Marinho, M. T. M. C. Cunha, G. Thomas and J. M. Barbosa-Filho, Fitoterapia, 65 (1994) 475.
2 J. M. Barbosa-Filho, D. F. Medeiros and J. Bhattacharyya, Ciência Cultura Saúde, 3 (1981) 35.
3 T. Ozawa, Bull. Chem. Soc. Japan, 38 (1965) 1881.
4 A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.
5 P. M. Madhusudanan, K. Krishnan and K. N. Ninan, Thermochim. Acta, 221 (1993) 13.
6 H. H. Horowitz and R. Metzger, Anal. Chem., 35 (1963) 1964.
7 Van Krevelen, C. Van Heerden and F. Hutjens, Fuel, 30 (1951) 253.
8 The Merck Index, An Encyclopedia of Chemicals, Drugs and Biologicals, 12th Ed., Merck and Co., Inc. Whitehouse Station, N. J. 1996.