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Chemical Characterization Of The Essential Oil Of The Floral Bud Of "Pequi" (*Caryocar Brasiliense* Camb)

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ABSTRACT

This paper describes the isolation of the essential oil from the floral bud of *Caryocar brasiliense* ("pequi") by steam distillation. The chemical characterization was performed by mass spectrophotometry coupled with gas chromatography. Eudesmol (39.18%), 2-methyl-3-hydroxypropanoic acid (4.35%), 2-(3-bromopropyl)-cyclohexanone (2.48%) and cis-farnesol (3.98%) were detected in the essential oil of the floral bud. The essential oil content was 0.06%.

KEYWORDS

Caryocar brasiliense;
Essential oil;
Floral bud;
Composition;
Pequi;
Souari nut.

INTRODUCTION

The souari nut tree ("pequi") is an arboreal plant of the *Caryocaraceae* family, genus *Caryocar* L., which includes about 20 species. At least eight species of this genus occur in Brazil, most being large plants that comprise part of the vegetation of the Amazon forest. Two species are important outside the limits of the humid tropical Amazonian forest: *C. coriaceum* Wittm., encountered in the fields of the Northeast and the *C. brasiliense* Camb., which is one of the most plentiful species in Central Brazil. It is a species typical of the woody "cerrado" region. Etymologically, the name "piqui", "piquiá" or "pequi" originated from the Tupy language (py = coat; qui = thorn), signifying thorny coat, probably because the kernel of the fruit is coated with fine thorns[1]. The souari nut tree is a species extensively utilized by the populations of the Cerrado region. All of its parts - wood, tannins, seed oil, fruit pulp and leaves - have specific uses[2-8]. Araujo[9] has reviewed the economic value of the plant.

Note

However, the principal use of the fruit is as food. It is extensively consumed by the population of the region because of its high nutritional value. The physical characteristics and mineral content have been detailed by Nascimento et al[10].

The souari nut tree has not been extensively studied phytochemically. Studies by Oliveira et al[11]. led to the isolation of friedelin, friedelanol and oleanolic acid from the ethanol extract of the leaves through re-extraction with hexane and chloroform. Acid catalyzed hydrolysis of the ethanol extract of the leaves furnished β-sitosterol and stigmansterol (mixture), followed by β-amirina and oleanolic acid. Eleagic acid was isolated from a chloroform-insoluble fraction.

The oils from the fruits and seeds were analyzed by gas chromatography. Recently, the chemical composition of the essential oils of the leaves and seeds of *Caryocar brasiliense* was studied using steam distillation with a Clevenger apparatus[12]. The principal components identified in the fruit were methyl hexanoate, propyl tiglate, ethyl octanoate and methyl pentanoate. The components isolated from the leaves were octanosane, heptadecene and isoamyl dodecanoate. These results were somewhat different from those obtained by Passos et al.,[13] who observed that the major component of the seed oil was the ethyl hexanoate and those of the leaves were octacosane, heptadecane and hexadecanol.

MATERIAL AND METHODS

The closed floral buds were collected from a population of native souari nut trees located in the municipality of Itumirim, MG, Brazil. The identification of the species was performed by comparison with material present in the Herbário ESAL (Herbarium of the Departamento de Biologia of the Universidade Federal de Lavras - UFLA). A specimen of the species collected at the location under study was incorporated into the herbarium, receiving the registration number 16.118.

A 68 g portion of dried floral buds was submitted to steam distillation for 1.5 hr, producing 1.5 L of distillate. The distillate was extracted with dichloromethane. The organic fractions were united and dried over anhydrous $MgSO_4$. The mixture was filtered and evaporated on a rotary evaporator. The oily residue was analyzed by gas chromatography coupled with a mass spectrometer (GCQ-Finnigan) equipped with a capillary column containing an apolar stationary phase. The eluted components were identified by their mass spectra, these being compared to those of known compounds encountered in the literature.

Eudesmol (RT = 21.12 min): m/e (%) 51(1.6), 53 (6.3), 54 (1.6), 55 (14.1), 57 (2.3), 59 (100.0) $[(CH_3)_2C=OH]^+$, 60 (3.9), 65 (3.9), 67 (18.0), 68 (5.5), 69 (8.6), 71 (2.3), 77 (7.8), 78 (2.3), 79 (16.4), 80 (5.5), 81 (19.5), 82 (14.8), 83 (4.7), 91 (11.7), 92 (2.3), 93 (15.6), 94 (6.3), 95 (13.3), 96 (4.7), 97 (1.6), 105 (10.2), 106 (2.3), 107 (14.8), 108 (21.9), 109 (14.1), 110 (2.3), 119 (3.9), 120 (1.6), 121 (9.4), 122 (9.4), 123 (7.8), 133 (4.7), 135 (4.7), 147 (2.3), 149 (20.3), 150 (3.1), 161 (3.9), 164 (7.8), 165 (1.6), 189 (3.1), 204 (2.3) $[M-H_2O]^+$.

2-Methyl-3-hydroxypropanoic acid (RT = 21.95 min): m/e (%) 55 (23.6), 56 (92.5), 57 (21.7), 69 (17.0), 71 (100.0), 72 (7.5), 73 (13.2), 85 (9.4), 89 (49.1) $[m-15]^+$.

cis-Farnesol (RT = 18.81 min): m/e (%) 53 (30.0), 55 (76.0), 57 (18.0), 59 (37.0), 65 (18.0), 67 (71.0), 69 (100.0), 71 (26.0), 77 (32.0), 79 (63.0), 80 (12.0), 81 (76.0), 82 (30.0), 83 (19.0), 91 (56.0), 92 (12.0), 93 (72.0), 94 (20.0), 95 (42.0), 96 (18.0), 105 (63.0), 106 (18.0), 107 (82.0), 108 (30.0), 109 (52.0), 119 (36.0), 121 (33.0), 122 (27.0), 133 (23.0), 135 (19.0), 147 (18.0), 148 (13.0), 149 (13.0), 161 (36.0), 163 (15.0), 189 (14.0).

2-(3-Bromopropyl)-cyclohexanone (RT = 24.04 min): m/e (%) 53 (29.7), 55 (90.1), 56 (22.5), 57 (21.6), 59 (36.0), 65 (14.4), 67 (55.9), 68 (10.8), 69 (66.7), 71 (42.3), 77 (29.7), 79 (48.6), 81 (100.0), 82 (18.0), 83 (61.3), 84 (11.7), 91 (34.2), 93 (74.8), 94 (13.5), 95 (81.1), 96 (13.5), 97 (19.8), 105 (19.8), 107 (56.8), 108 (25.2), 109 (35.1), 111 (30,6), 119 (13.5), 121 (63.1), 122 (16.2), 123 (14.4), 139 (82.9), 165 (11.7), 178 (37.8).

RESULTS AND DISCUSSION

The yield of the essential oil from the floral buds

Note

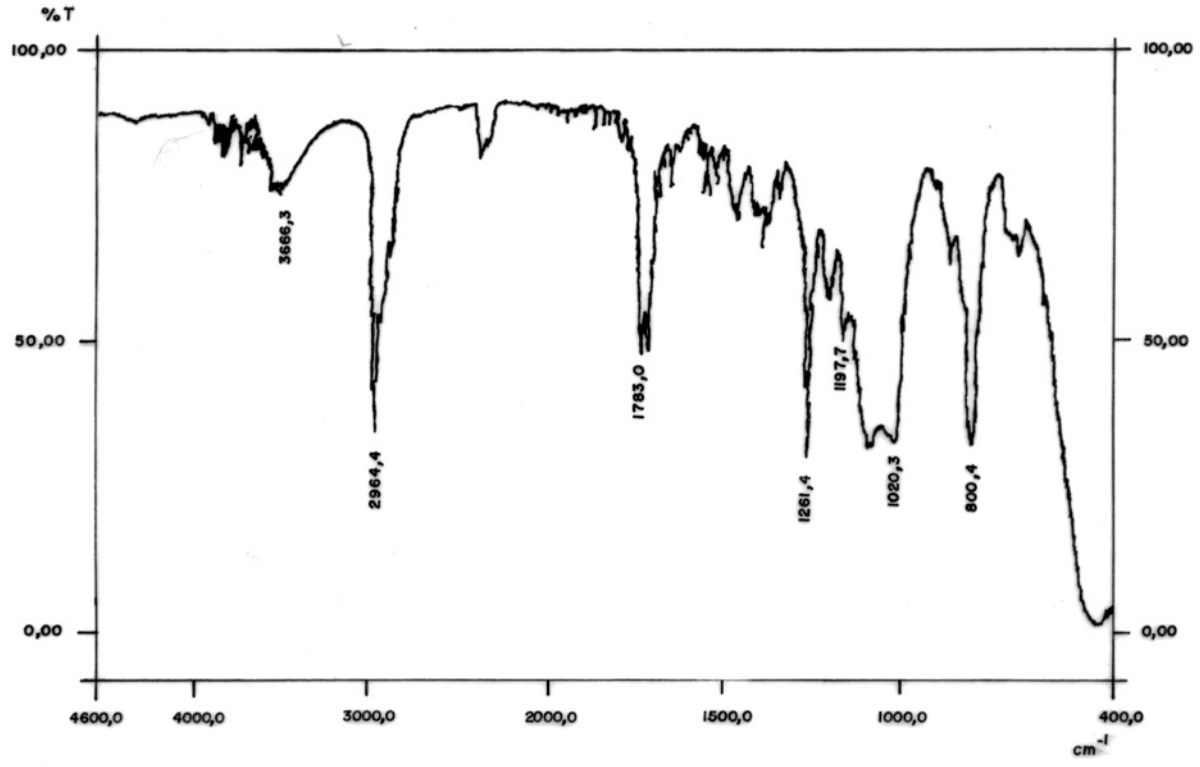

Figure 1: Infrared spectrum of the essential oil from the floral bud of *Carycar brasiliense* Camb.

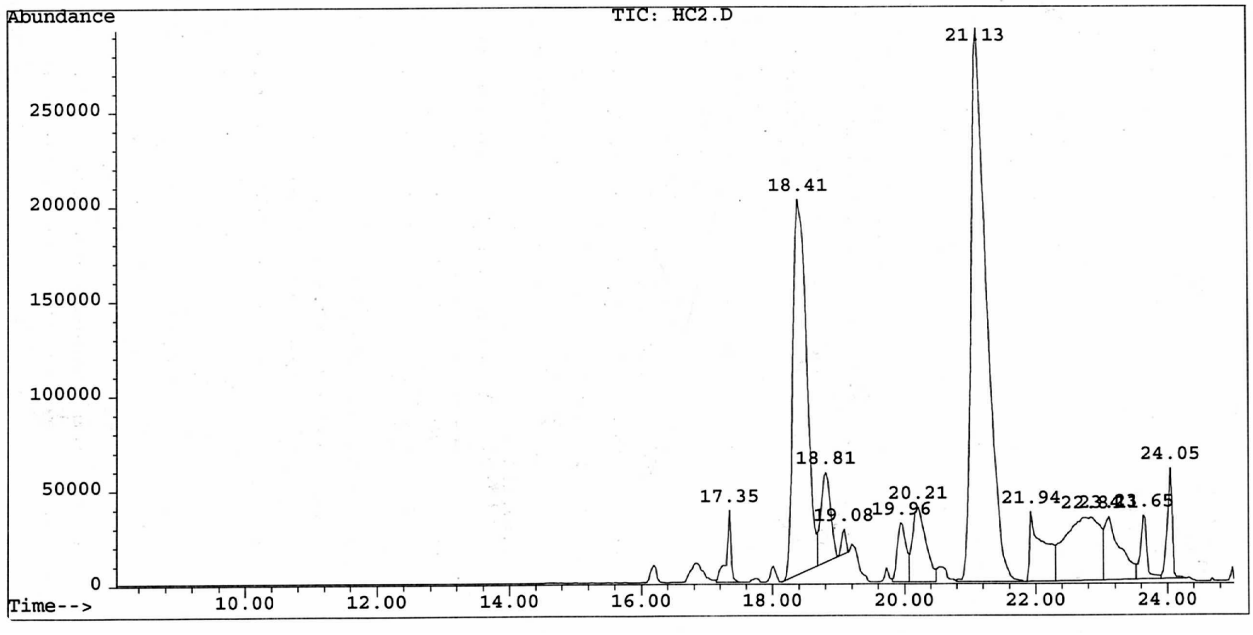

Figure 2: Chromatogram of the essential oil from the floral bud of *Carycar brasiliense* Camb.

was 0.06%. The presence of two peaks centered at 1783 and 1716 cm^{-1} in the infrared spectrum of this oil, characteristic of the carbonyl group, could be due to carboxylic acids, although the band near 3500 cm^{-1}, corresponding to the OH stretching vibration, was weak (Figure 1). The carbonyl stretching absorp-

Note

TABLE 1: Principal substances encountered in the essential oil from the floral bud of *Carycar brasiliense* Camb (GC/MS).

Retention time (min)	Relative area (%)	Substance suggested by the library	Ref.	Probability of identity (%)
21.12	39.18	Beta-eudesmol	45034	91
			45032	83
			129911	83
18.42	23.46	(-)-Beta-elemene	36668	43
		Trans-caryophylene	128692	38
		Trans-caryophylene	128686	35
20.21	4.56	Calarene	128759	86
		Hedicariol	44977	83
		Elemol	129878	72
21.94	4.35	2-Methyl-3-hydroxypropanoic acid	129454	45
18.81	3.98	*Cis*-farnesol	44953	38
		(Z,E)-5,10-Pentacadien-1-ol	46003	35
24.04	2.48	3-Methyl-2-cyclohexen-1-one	8944	38
		Spiro[4,5]decan-6-one	137773	27
		2-(3-Bromopropyl)-cyclohexanone	42561	25
23.66	1.95	Beta-citronelol	124532	38
		Beta-citronelol	124533	38
		E-6-Dodecenylacetate	46801	35

tion could also be a result of the presence of other compounds such as esters. Inflections around 1683 to 1635 cm^{-1} may be characteristic of non-conjugated double bonds. Absorptions at 1261 and 1020 cm^{-1} could be a result of the C-O stretching vibration of primary, secondary or tertiary alcohols. The sharp bands at 1683 and 1470 cm^{-1}, the presence of harmonics between 2000 - 1800 cm^{-1} and a well-defined absorption at 800 cm^{-1} could indicate the presence of the C=C bond of a *para*-substituted aromatic ring.

Thirteen different compounds were encountered in the chromatogram of this oil (Figure 2). These compounds are shown in TABLE 1. In general, the compounds were terpenes, especially sesquiterpenes, containing alcohol, ketone, carboxylic acid and ester groups. The data in TABLE 1 show that the essential oil from the floral buds contained a principal component that corresponded to 39% of the total content. GC/MS analysis indicated that this compound was eudesmol. The mass spectrum of this compound (RT = 21.12 min) confirmed this result. This substance had a molecular weight of 222 g/mole, being a long chain cyclic hydrocarbon with a tertiary alcohol group and methyl branches. Although the molecular ion was not detected, as is common with tertiary alcohols, the peak at m/e 204 can be explained by the loss of a molecule of water, also common in alcohols. The fragmentation of alcohols bearing methyl branches, such as terpenoid alcohols, results in a reasonably strong peak at M - 33, resulting from the loss of the methyl group and water. In this case, this peak appears at m/e 189. The base peak (m/e 59) resulted from the cleavage of the C-C bond next to the oxygen, as is shown in figure 3. The fragmentation typical of hydrocarbons is characterized by the sequence of fragments separated by 14 atomic mass units. The highest peak in each group corresponded to the fragment C_nH_{2n+1}, generally accompanied by the fragments C_nH_{2n} and C_nH_{2n-1}.

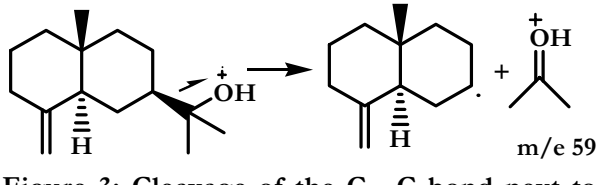

Figure 3: Cleavage of the C—C bond next to the hydroxyl group of eudesmol (1).

The peak with RT = 21.95 min corresponded to 2-methyl-3-hydroxypropanoic acid (MW = 104 g/mole), constituting 4.35% of the essential oil (TABLE 1). Its mass spectrum (Figure 4) confirmed this observation. Since it contains a primary alcohol and carboxylic acid groups, its mass spectrum would

Note

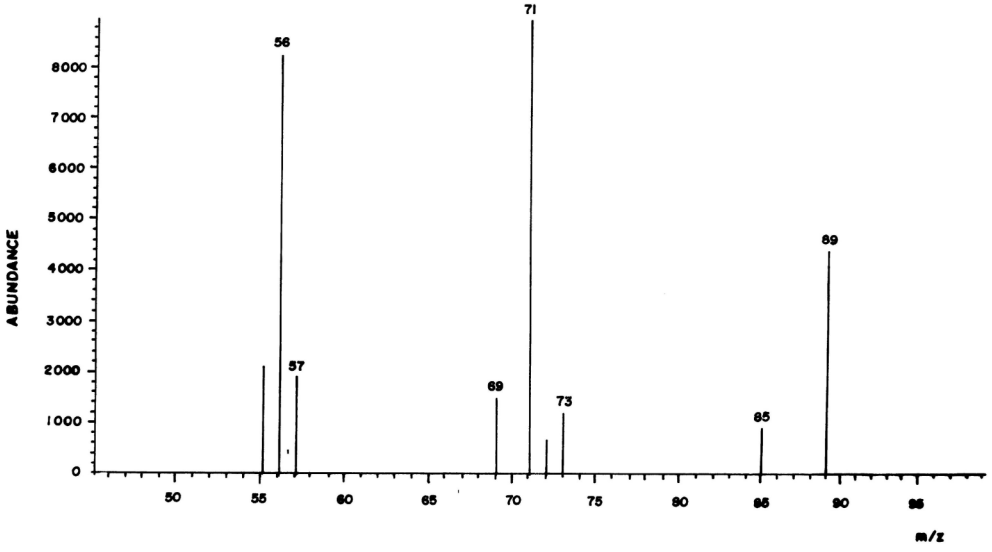

Figure 4: Mass spectrum of the substance eluted with a retention time equal to 21.95 min.

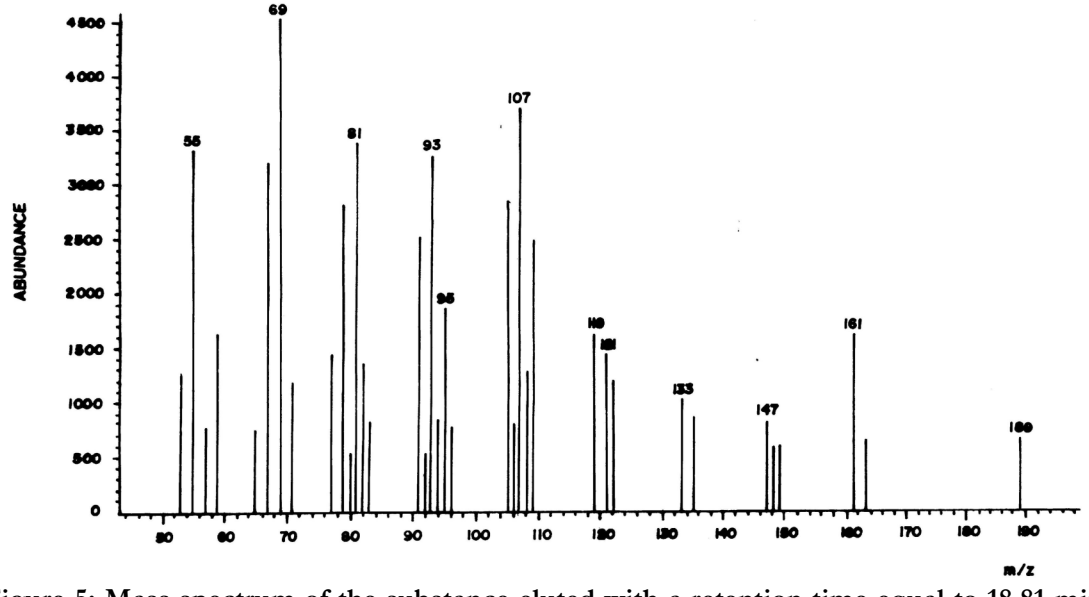

Figure 5: Mass spectrum of the substance eluted with a retention time equal to 18.81 min.

show fragmentations characteristic of these two functions. Thus, the fragment at m/e 89 could be explained by the cleavage of the methyl branch (M - 15). The peak at m/e 71 min would be a result of loss of CH_3 and H_2O, characteristic of branched alcohols containing methyl groups. And the fragment at m/e 73 would resulted from the loss of the CH_2OH group, while the peak at m/e 56 corresponded to the loss of a CH_3 group and H_2O from the m/e 89 fragment.

According to the instrument data bank, the peak with RT = 18.81 min corresponded to *cis*-farnesol (MW = 222 g/mole) or 5,10-(Z,E)-pentacadien-1-ol (MW = 224 g/mole). However, the mass spectrum corresponding to this peak (Figure 5) presented a cleavage typical of branched alcohols containing methyl groups, indicating that the substance was *cis*-farnesol. As with eudesmol, a reasonably strong peak was observed at M - 33 (m/z 189), resulting from the loss of CH_3 and H_2O. The remaining peaks are typical of long chain (> six carbons) alcohols whose spectrum is dominated by the sequence of fragments

Note

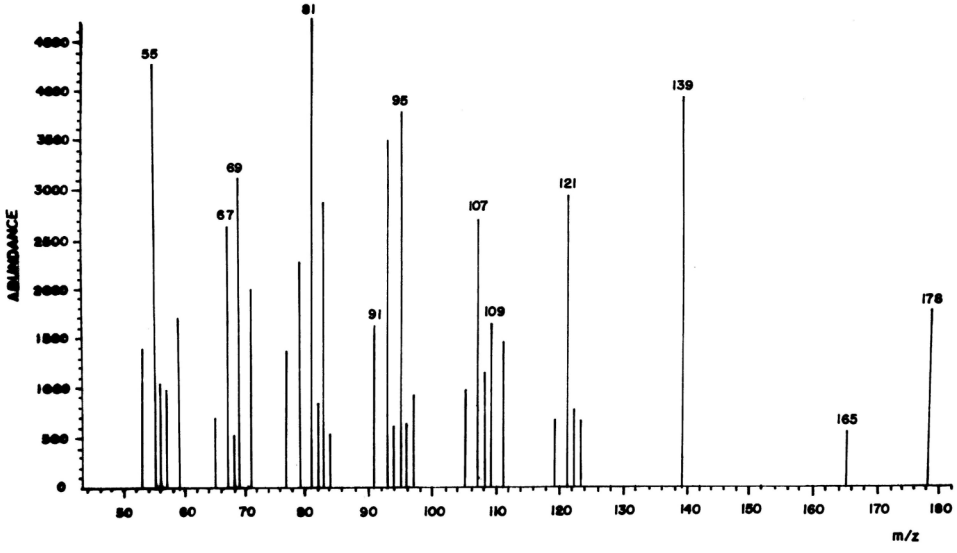

Figure 6: Mass spectrum of the substance eluted with a retention time equal to 24.04 min.

separated by 14 atomic mass units.

Three possible structures were suggested for the peak with RT = 24.04 min: 3-methyl-2-cyclohexene-1-one (MW = 110 g/mole); spiro-[4,5]-decan-6-one (MW = 152 g/mole) and 2-(3-bromopropyl)-cyclohexanone (MW = 218.9 g/mole). However, peaks with m/e = M+2 and M+4 were prevalent in the spectrum (Figure 6), a fact that indicates the presence of a halogenated substance, especially one containing bromine. The fragment with m/e 139 could result from the loss of bromine and the peaks with m/e 79 and 81 corresponded to the fragment Br^+. The peak at m/e 55 would result from the rearrangement of hydrogen with formation of a secondary radical and fragmentation of the cyclohexanone intermediate[14].

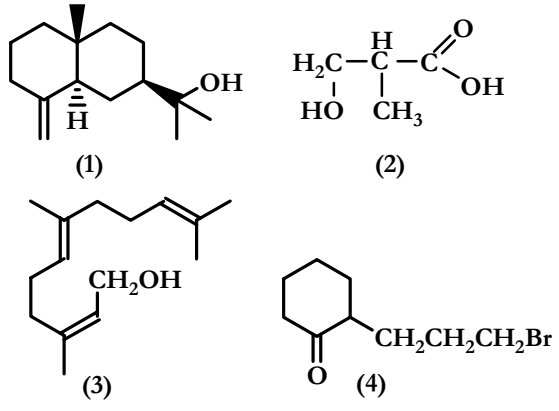

Figure 7: Principal components identified via analysis of the mass spectra: eudesmol (1), 2-methyl-3-hydroxypropanoic acid (2), cis-farnesol (3) and 2-(3-bromopropyl)-cyclohexanone (4).

CONCLUSION

The principal compounds obtained from the floral bud of *C. brasiliense* and identified through their mass spectral data were eudesmol (1), 2-methyl-3-hydroxypropanoic acid (2), *cis*-farnesol (3) and 2-(3-bromopropyl)-cyclohexanone (4) (Figure 7).

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Note

REFERENCES

[1] Brasil, Ministério da Indústria e do Comércio. Secretaria de Tecnologia Industrial, Produção de combustíveis líquidos a partir de óleos vegetais. Brasília: STI/CTI, 163 **(1985)**.

[2] E.P.Heringer; Belo Horizonte, 113-118 **(1962)**.

[3] P.V.Silva Filho; Informe Agropecuário, **16**, 27-32 **(1992)**.

[4] E.C.Silva; Desenvolvimento de emulsões cosméticas utilizando o óleo de pequi (Caryocar brasiliense Camb.). Masters Thesis, Universidade de São Paulo, São Paulo, 112 **(1994)**.

[5] S.P.Almeida, C.E.B.Proença, S.M.Sano, J.F.Ribeiro; Cerrado: espécies úteis, EMBRAPA-CPAC, Planaltina, 106 **(1998)**.

[6] G.Franco; 'Nutrição: Texto Básico e Tabela de Composição Química Dos Alimentos', 6 Ed. Livraria Atheneu, Rio de Janeiro, 230 **(1982)**.

[7] M.M.Barradas, W.Handro; Sobre os óleos do fruto e da semente do piqui–Caryocar brasiliense Camb. (Caryocaraceae). In: Simpósio Sobre o Cerrado 3: São Paulo, SP, São Paulo, Ed. Blucher/USP, 110-113 **(1971)**.

[8] J.R.Paula, B.H.N.Sales, S.C.Santos, C.M.A.Oliveira, L. M.Lião, P.H.Ferri, H.D.Ferreira; Composição química dos óleos essenciais das folhas e frutos de Caryocar brasiliense Camb. (Pequi). In: Reunião Anual da Sociedade Brasileira de Química, 23: Poços de Caldas: Sociedade Brasileira de Química, **2**, PN007 **(2000)**.

[9] F.D.Araujo de; Economic-Botany, **49(1)**, 40-48 **(1995)**.

[10] V.M.Nascimento, A.A.Xavier, L.S.Correa, W.V.Valerio Filho; Acta-Horticulturae, **370**, 113-116 **(1995)**.

[11] M.M.Oliveira, B.Gilbert, W.B.Mors; Anais da Academia Brasileira de Letras, **40**, 451-452 **(1968)**.

[12] M.C.S.Marques, Cardoso M.das G., P.E.de Souza, M.L.Gavilanes, J.A.de Souza, N.E.Pereira, I.de O.Negrao; Ciencia e Agrotecnologia, **26**, 1410-1419 **(2002)**.

[13] X.S.Passos, A.C.M.Castro, J.S.Pires, A.C.F.Garcia, F.C. Campos, O.F.L.Fernandes, J.R.Paula, H.D.Ferreira, S. C.Santos, P.H.Ferri, R.R.M. do Silva; Pharmaceutical Biology, **41(5)**, 319-324 **(2003)**.

[14] R.M.Silverstein, G.C.Bassler, T.C.Morril; 'Identificação Espectrométrica de Compostos Orgânicos', Guanabara Dois, Rio de Janeiro, 387 **(1994)**.