The Composition of Blackcurrant Absolute (Ribes Nigrum)

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The blackcurrant bush is grown extensively in central and northern Europe for its berries, which are generally used in jellies and as flavours for ice creams, yoghurts and alcoholic beverages. In some regions, especially in Burgundy, the bushes are pruned during the winter months. The cuttings already contain the hibernating buds. These buds, in the form of alcoholic tinctures, were used for a long time to enhance the flavour of the juice of the berries, especially after the juice had been stored for a few months.

In the last decade, an important portion of the buds also has been converted into an absolute. The solvent extraction yields 2-4% of a concrete, which gives about 80% of the absolute. This absolute serves largely the same purpose as the alcoholic infusion, namely as flavour enhancer, and in recent years is also used as a major ingredient in some luxury fragrances.

The absolute, in the form of a dark green paste, has a very characteristic, penetrating and powerful odour.

The relatively high price of the absolute is readily explained by the extremely high labour intensity of the bud harvest. It takes a skilled worker about five hours to cut the buds off the twigs or around 200 hours of cutting time per kilo of absolute.

The literature contains only a limited number of studies devoted to the composition of blackcurrant buds extract, the most important being by Fellous (1974) and Latrasse and Lautin (1977).

Source of the Samples

In our study we employed three different products, an absolute obtained in the laboratory from buds grown in Burgundy of the "Noir Bourgogne" variety; another laboratory produced absolute from buds collected in Kent, England, from the local variety "Baldwin"; and an industrial produced absolute from buds from various regions of France and elsewhere.

Characteristics of the Absolutes

The physical contents given in Table I of the three absolutes are in close agreement with each other and are characterized by an important presence of acids and a low content of esters.

The essential oils (12-15%) obtained by steam distillation of the absolutes, in the form of pale mobile liquids having the typical powerful odour of the absolutes and the almost odourless residues are examined separately.

The Nonvolatile Fraction of the Absolute

The nonvolatile fraction of the absolute represents about 80% of the total in the form of a dark green, almost odourless paste having an acid index of over 150. The high content of free acid and the ones obtained after saponification allows us to divide this fraction into two groups as seen in Table II.

The unsaponifiable portion obtained either by liquid-liquid extraction or ion-exchange resin separation represents only 10% compared with 90% acid fraction. The two groups are studied separately. A preliminary study by T.L.C. on silica gel of neutral fraction gives identical patterns for the three products under study. One is able to distinguish in the acid fraction 4 groups of constituents (A to D) and 5 groups in non-saponifiable part (I to V). In total fraction before saponification one finds a partial super-imposition of the acids and the un-saponifiable material (see figure 1).

A systematic study by high pressure liquid chromatography (HPLC) and thin layer chromatography (TLC) on silica gel allows the isolation identification of a number of the elements of the two groups.

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Table I. Physico Chemical Contents of Blackcurrant Buds Absolute

	C.A.	C.F.	C.D.
Acid Value	119	125	123
Ester Value	9	11	21
% Composition of Esential Oil	15	12	13

C.A.—Cassis Anglais
C.F.—Cassis Francais
C.D.—Cassis Francais d'origines diverses

Constituents of the Non-Saponifiable Fraction

The above mentioned 4 groups, separated by HPLC, have been studied with a glass capillary column (OV.17), of 40 m. length at 270°. The hydrocarbons were injected directly and the alcohols in the form of their trimethylsilyl ethers. The compounds were identified by means of infrared (IR) and nuclear magnetic resonance (NMR) and by their relative retention times in the gas liquid chromatography (GLC).

Product I (Rf = 1) represents a complex mixture of linear and branched hydrocarbons superior to C_{20} which did not steam distill.

Product II (Rf = 0.8) is a mixture of more than 50 individual products in the form of linear and branched alcohols of C_{10} or higher and terpene alcohols. This fraction is quantitatively the most important one and in the absolute it is present in the form of an ester, principally of the fatty acids.

Product III (Rf = 1.7) is present in a minor amount consisting of methyl sterols, chiefly lanosterol.

Product IV (Rf = 0.6) consists chiefly of sterols, particularly β-sitosterol. The composition of this part is fairly typical for a vegetable extract of this nature.

Campesterol—1.9%
Stigmasterol—2.1%
β-Sitosterol—88.4%
Δ_5 Avenasterol—1.0%
Δ_7 Stigmasterol—0.5%
Δ_7 Avenasterol—6.1%

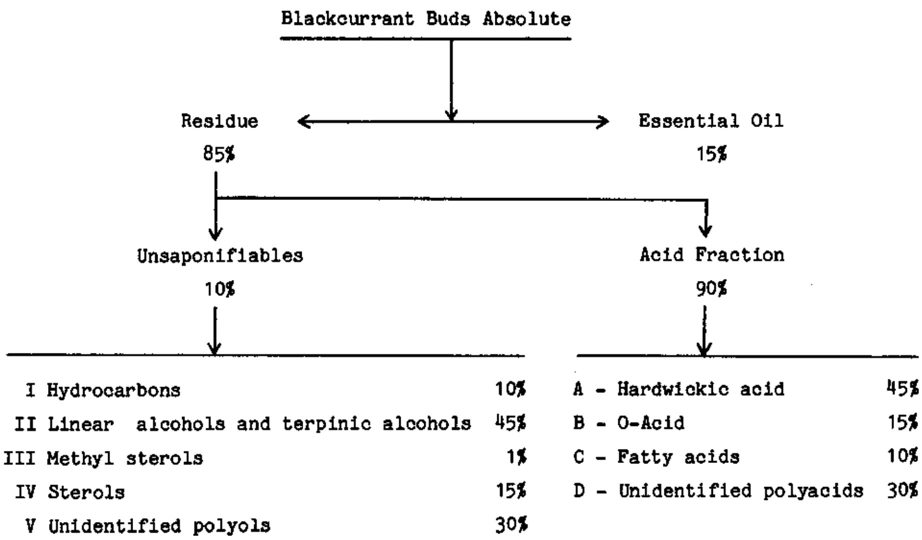
Main Constituents of the Acid Fraction

The two groups A and B, isolated by HPLC, have been identified by MS, IR and NMR. The fatty acids of group C have been identified by the relative retention times of their methylesters on a GLC glass capillary column (carbowax 20 M) of 50 m.

Product A (Rf = 0.7) is an acid with a composition of $C_{20}H_{28}O_3$ and having a structure (see figure 2) which is in agreement with the spectral analysis. This acid, known under the name of Hardwickic acid, has already been isolated by Fellous et al. from benzene extracts of blackcurrant buds. This is the major substance of the acid fraction where in free form it represents up to 40%. The stereochemical structure will be published later.

Product B (Rf = 0.5), an acid, has a formula of $C_{21}O_4H_{28}$ (see figure 3). Its structure is consistent with the spectral results. This acid, to the best of our knowledge, has not yet been described in the blackcurrant absolute. In this connection it

Table II.



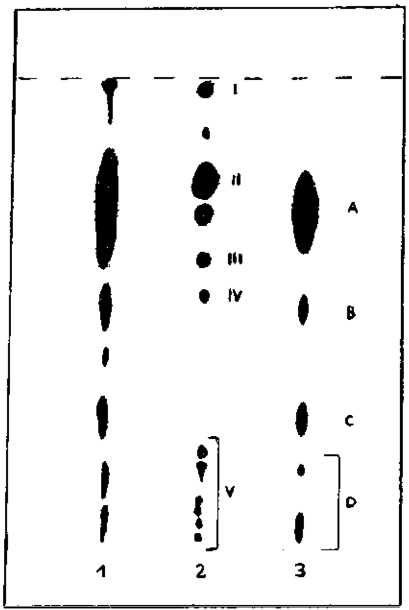


Figure 1
Silica-Gel-Coated T.L.C. Plates
Solvent:
Methylene Chloride 9
Isopropylic Ether 1
Revelation: Sulfomolybdic
1—Rough Product Before Saponification
2—Unsaponifiables
3—Acid Fraction

should be noted that Wright (1975) has reported the presence of important amounts of abscisic acid ($C_{15}H_{20}O_4$). We could not find any detectable level of this acid in the absolutes studied.

Product C (Rf = 0.3) is a mixture of fatty acids in types and proportions typical of vegetable extracts of this type. In the absolute they are present in the form of esters of the alcohols and sterols identified in the unsaponifiable fraction (see composition of sterols from blackcurrant buds absolute above).

The Volatile Part (Essential Oil)

The physical and chemical constants of the volatile part of the absolute are summarized in Table III, showing a relatively low content of acids and esters.

The GLC with a 60 m glass column (carbowax 20 M) reveals a highly complex blend of over 150 detectable substances. The principal peaks, about 20, representing over 85% of the essence have been identified by standard instrumental techniques (GLC coupled with MS).

Considering that three samples had not exactly the same raw material source as far as the variety of the plant and growing conditions are concerned and also considering the complexity of the oil composition, there is nevertheless a reasonable similarity between the three samples as indicated in Table II. We confirm the neat separation between the monoterpene group amounting to 50-60% (see Table IV) and the

Table III. Physico Chemical Contents of Blackcurrant Buds Essential Oil

	C.A.	C.F.	C.D.
Acid Value	1.0	0.9	1.1
Ester Value	3.0	4.5	5.0
Density (20° C)	0.8742	0.8780	0.8762
Refractive Index (n_{20})	1.488	1.492	1.483
Specific Rotation (alpha)$^{20}_{D}$	+ 2.85	+ 2.84	+ 2.84

C.A.--Cassis Anglais
C.F.--Cassis Francais
C.D.--Cassis Francais d'origines diverses

Table IV. Relative Percentage Composition of Principal Constituents of Blackcurrant Buds Oil

Monoterpenes

Peak No.	Identification	C.F.	C.A.	C.D.
4	alpha-Pinene	1.5	1.4	2.4
5	beta-Pinene	0.3	0.2	0.4
6	Sabiene	3.7	2.8	1.8
8	delta$_3$-Carene	14.5	13.0	19.0
9	Myrcene	2.2	2.2	3.8
11	alpha-Terpinene	0.7	1.2	2.7
13	Limonene	4.9	3.7	3.8
14	beta-Phellandrene	6.1	4.9	10.0
15	cis-Ocimene	1.5	1.5	1.6
16	gamma-Terpinene	2.8	2.0	1.0
17	trans-Ocimene	0.6	2.1	2.5
18	Octanone-3	0.7	0.7	1.8
20	para-Cymene	6.3	4.3	1.9
22	Terpinolene	3.9	6.6	10.9
23	X	2.0	2.0	1.1

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Table V. Relative Percentage Composition of Principal Constituents of Blackcurrant Buds Oil

Sesquiterpenes

Peak No.	Identification	C.F.	C.A.	C.D.
43	Octene 1-ol 3	0.1	0.15	0.1
46	alpha-Copaene	0.6	0.4	0.2
68	beta-Elemene	0.4	0.5	0.4
69	Caryophyllene	9.3	14.0	9.0
70	X	2.4	1.1	2.3
71	Terpinene 1-ol 4	3.7	6.3	2.4
78	alpha-Humulene + Acetate de Citronellyle	1.5	4.5	1.7
106	Y	4.3	2.5	0.7
127	Z	4.5	1.6	0.25
146	V	5.3	1.1	0.8

C.A.--Cassis Anglais
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heavier fraction dominated by β caryophyllene and terpene—1—01—4 (see Table V) already reported by Williamson (1972). The monoterpenes have been completely identified and our findings confirm those of Latrasse and Blandin.

Figure 2

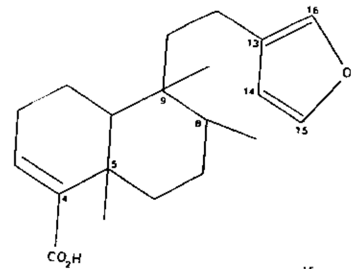
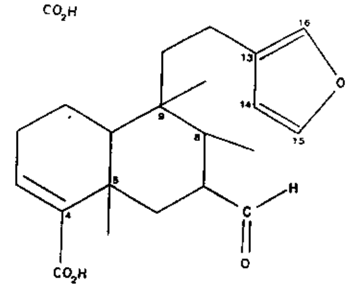


Figure 3



It is clear that the monoterpenes present in this odourous volatile fraction of the absolute cannot account for the typical and potent odour of the liquid. This can be readily demonstrated by the monoterpene fraction isolated by liquid chromatography that lacks the characteristic odour completely.

On the other hand, one detects this note clearly in the more polar and extremely complex mixture eluded after the β-caryophyllene. Also in this zone one observes clear differences in minor components between the three samples under study. It is generally assumed that the characteristic note of the blackcurrant buds is due to the presence of sulfur-containing compounds and indeed the absolute contains between 0.08-0.15% of sulfur.

We know further that the totality or near totality of the sulfur-containing substances are in the sesquiterpene section. Unfortunately, due to the extreme complexity of this fraction and the very low content of the individual constituents we have not yet been able to isolate in a satisfactory manner the compound or compounds being responsible for the typical odour of this extract.

On the other hand, the ratio between this compound and the total level of surfur present does imply the presence of at least one more sulfur-containing compound, more likely several.

We continue our research.

References

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