Chapter 14

The Benzyl Esters and Benzoates

BENZYL alcohol (phenyl carbinol or phenylmethyl alcohol) has a fairly wide natural occurrence in small quantities in the free state and in various ester combinations. The refined qualities of the synthetic alcohol which are used in perfumery are practically odourless, and its value lies in its versatility as an all-round fixative, solvent, diluent and blender. It shares with tolulene, first distilled from balsam of tolu, a similar origin, namely, by the processing of gum benzoin, which also yields benzoic acid upon sublimation.

Benzoic acid (benzene carboxylic acid or phenylformic acid) is interesting in many ways. It occurs in the free state, in gum benzoin, styrax, Peru, tolu and similar balsams, in " dragon's blood " and many other tropical shellac-like resins and gummy exudations; also it is associated with cascarilla, canella and similar incense or fumigating powder barks and, finally, is found in the sap of such plants as the American spikenard, golden rod and eagle vine.

In this direction it is seen that the basic odour associated with these items, when examined as *materia medica* specimens, is mildly balsamic, but when the latent odour is liberated by slow combustion, either by heaping fragments of the dried materials upon live charcoal or mixed with sufficient saltpetre to form a slowly smouldering mixture, the characteristic " incense-like " odours of the mixed benzyl and cinnamyl radical esters becomes evident in the fragrant smoke.

The almost inodorous benzyl alcohol is featured in all the semi-exotic bloom perfumes, such as acacia, azalea, carnation, cassie, gardenia, jasmin, hyacinth, neroli, tuberose, wallflower and ylang; the fragrance of these being assisted to a considerable extent by the simultaneous presence of the acetic ester; but it is also interesting to note how frequently in the above sequence the presence of the benzoic, cinnamic and salicylic esters of methyl alcohol contribute to, or support, the dominant note of each blossom.

Compared with the extremely mild odours of commercial benzyl

alcohol and benzoic acid, the odour of the aldehyde bears no osmical relation to that of its progenitors, as is the case with almost every one of the other arylaldehydes; yet, on a more detailed examination of the oils of cajuput, cascarilla, cassia, cinnamon, clove, nutmeg and patchouli, in which traces of benzaldehyde occur, it is noteworthy just how closely the almond odour is interwoven and so well complements the different versions of the spicy motif peculiar to these oils. It is also interesting to note in this context that the almond-hawthorn complex is one of the four major divisions into which the fragrance of a large sector of common wild, garden and tropical flowers can be segregated.

At this stage, only the vegetable origin of benzoic acid has been considered, but like the indoles it also originates within the complexities of the animal metabolism. Take castoreum, for instance. Bearing in mind that the chief item of the diet of the beaver is the tender bark and shoots of the birch and poplar trees, which contain large amounts of a glucosidal combination of ortho-hydroxybenzoic acid (salicylic acid), hence by hydrolysis and complex interesterification *in vivo*, many cross benzyl and salicyl linkages result and add their odour quanta to the hundred or so items which constitute the physical vehicle and osmical build-up of castoreum.

Another interesting sidelight is found in a consideration of equine urine, in which benzoic acid in combination with glycocoll, appears as hippuric acid (benzamino-acetic acid), which upon acid hydrolysis yields free benzoic acid. It may be noted in passing, from the pharmacopoeias and wholesale drug lists of the last century, that *Acidum Benzoicum ex urina* was placed against *Acid. Benzoic ex gum*, and *Ac. Benz. ex toluole*.

In surveying the properties of the benzoates as perfume components, the interweaving of the aryl and aliphatic radicals produces some interesting results and provides a wide selective choice, but it will be seen that the majority of the items discussed are only used in comparatively small quantities, and then chiefly to emphasise effects already apparent in the build-up of the perfume formula.

In so far as concerns the alkyl benzoates, the interest is centred upon the usage of large percentages of the wintergreen aromas of methyl and ethyl benzoates for soap and industrial perfumes; and also upon amyl benzoate, which may be coupled with practically odourless

benzyl benzoate, as a first-class fixative and general-purpose solvent for the crystallines, but more particularly as a means whereby the difficultly soluble nitro-musks may be available in a convenient and concentrated form, assisted on occasion by the supplementary aid afforded by benzyl alcohol and dibenzyl phthalate.

The value of the other aryl benzoates can only be assessed by regarding them as components of the " balsamic " aroma, which is of considerable value as a background in almost every type of the heavy Oriental and fantasy perfumes, but the balsamic nuance requires to be handled with discretion if embodied into the purely floral conceptions.

In general, the terpene alcohol benzoates average about the usual 90% ester content, but in my opinion, although I have given suggestions regarding usage, which I have found practicable, yet, to reiterate, I think there is a certain degree of osmical incompatibility between the basic floral note of these alcohols and the balsamic element, and although rendered " aromatic," considerable care must be exercised in order to prevent a reversion of the floral element to the odour characteristic of " Friar's Balsam."

In conclusion, this first tabulation of the aryl derivatives does not indicate any outstanding departure from the set-up of the previous alkyl selections, the fruity and floral pattern still being prominent, while there is some initial emphasis upon the presence of the wintergreen and balsamic nuance. Finally, upon the question of stability, generally speaking, the benzoates show little or no trace of any upsetting acid dissociation, either upon storage or after incorporation in a composition.

BENZYL ESTERS
(Aliphatic)

BENZYL FORMATE—*See under Formates.*

BENZYL ACETATE—*See under Acetates.*

BENZYL PROPIONATE—*See under Propionates.*

BENZYL BUTYRATES—*See under Butyrates.*

BENZYL VALERIANATE—*See under Valerianates.*

BENZYL CAPROATE

Odour : A sweet apricot-jasmin note.

BENZYL HEPTYLATE

Odour : A fruity, herbal note resembling apricot-sage.

BENZYL CAPRYLATE

Odour : Similar to that of the heptylate, but somewhat dull and more fatty.

BENZYL PELARGONATE

Odour : A mild, slightly unctuous odour similar to that of Elemi oil.

Aromatic

BENZYL BENZOATE

Odour : When freshly distilled is practically odourless, but develops a faint balsamic-almond note on keeping.

Use : A versatile solvent for most crystallines, especially the nitro-musks. A general-purpose fixative. Stabiliser for the aliphatic aldehydes.

BENZYL PHENYLACETATE

Odour : Varies considerably, some samples being practically odourless while others have a sweet jasmin-rose note with a mellow honey-like undertone.

Use : Is useful rather as a fixative and body-builder, but may be used to advantage in the way suggested in the section dealing with phenylacetates.

BENZYL CINNAMATE

Odour: These crystals have a mild and very sweet balsamic odour which is very persistent.

Use : As detailed under the cinnamates, the outstanding usage is for face and talcum powders.

BENZYL SALICYLATE

Odour : Is almost odourless, but with age becomes somewhat balsamic.

Use : As for benzyl benzoate.

The Benzoates

METHYL BENZOATE—*See under Methyl Esters.*

ETHYL BENZOATE—*See under Ethyl Esters.*

N-PROPYL BENZOATE—*See under Propyl Esters.*

BUTYL BENZOATES—*See under Butyl Esters.*

ISO-AMYL BENZOATE—*See under Amyl Esters.*

N-HEXYL BENZOATE

Odour: Shows a very close simulation to the balsamic-sap aroma of freshly decorticated cypress twigs.

Use: Of particular value with labdanum for amber, chypre and leather perfumes, using from 5 to 10%.

PHENYL BENZOATE

Odour: Rose-geranium leaf.

Use: This crystalline substance is a useful fixative in soap compounds, etc.

BENZYL BENZOATE—*See under Benzyl Esters.*

N-HEPTYL BENZOATE

Odour: Has the damp green aroma of freshly bruised herbs.

Use: Usage is limited to tweed-heather and gorse-chypre compositions, at about 2%.

PHENYL-ETHYL BENZOATE

Odour: A sweet, soft rose with a slight balsamic undertone.

Use: Chiefly as a component, as well as a fixer, in rose compositions, using about 5%, but more particularly because of its property in rounding-off the initial pungency of the eugenols in carnation compounds, employing 3 to 7%.

N-OCTYL BENZOATE

Odour: A soft, fruity balsamic complex, possessing a mellowness not observed in other octyl esters.

Use: Up to 5% exhibits this mellowing property to good effect in chypre, fougère, woody bases, Middle East and Oriental perfumes.

CINNAMYL BENZOATE

Odour: A soft but deep spicy-balsamic note.

Use: As a fixer for most heavier types of perfumes and as a useful blender and modifier for such Oriental perfumes as the santal-rose and jasmin-vetivert Indian types, in which up to 10% may be incorporated.

PHENYL-PROPYL BENZOATE

Odour: Has a soft balsamic hyacinth-basil odour, closely approximating that of dahlia buds.

Use: Is rather a matter of experiment, but it can be used to useful purpose as a disseminator of methyl heptine and other alkyne carbonates in achieving remarkably natural foliage effects.

PHENYL-GLYCOL BENZOATE

Odour: A mild balsamic hyacinth-mimosa complex.

Use: Would appear to be of interest in lanolinated cold creams and similar skin foods, as even at 0.7% there is an agreeable muffling of the characteristic wool-fat odour.

NONYL BENZOATE

Odour: A complex resembling myrrh, with a faint background of sweet orange and a slight wintergreen undertone.

Use: About ½% can be used with advantage in réséda and mimosa bases, but its real value is as a *nuanceur* in fantasy compositions with high, mixed aldehydic topnotes.

ISO-BORNYL BENZOATE

Odour: Chiefly a balsamic pine, but more aromatic and herbal than the acetate or propionate.

Use: Somewhat limited; as an experimental variant in compositions where other Bornyl esters feature.

GERANYL BENZOATE

Odour: Has a deep, sweet, soft, aromatic rose-cananga cadence.

Use: A particularly useful fixer and blender in most red rose types, using up to 7%, but half as much again induces a remarkable deep velvety effect in lavender, fougère and chypre compositions.

LINALYL BENZOATE

Odour: A bergamot-lily-heather complex.

Use: A particularly useful fixer for tuberose, ylang and Oriental jasmin, at 3 to 5%, while double this quantity is useful as a starting point for "masculine" and outdoor perfumes of the tweed, heather, gorse and peat types.

TERPINYL BENZOATE

Odour: A fir tree-ylang, niobe complex.

Use: A good fixative for most soap perfumes, it can be used up to about 8% for simulating the lettuce and cucumber type of soap aroma.

CITRONELLYL BENZOATE

Odour: A mild, slightly aromatic, verbena-rose complex.

Use: Is particularly useful as a fixative and blender for most white rose types, using up to 6%, while half this quantity advantageously prolongs the aldehydic topnotes in exotic jonquil-hyacinth-lily compositions.

RHODINYL BENZOATE

Odour: Is a deeper version of the geranyl ester.

Use: Variation along the lines indicated for the geranyl derivative.

EUGENYL BENZOATE

Odour: A mild balsamic clove.

Use: Is of more value as a fixative, rather than any odour-complement, and is somewhat superior in this respect to benzyl iso-eugenol.

"Far below, flat and arid at our feet, gleaming with interlaced streams was the Alamut valley . . . Aziz . . . took me . . . downwards among steep slabs of granite where roses and jasmin and fragrant shrubs of many kinds gave us the same pleasure as to those earlier travellers who reported to Marco Polo seven centuries ago . . .

"We rode for some time along the stony bed of the stream, admiring the caper in flower which spreads there from boulder to boulder along the ground, and which they call the Unbelievers' flower, Kafir-gul. They use it in pilau."

"The boulders by the river were covered with mauve flowers belonging to some creeping plant, and in the damper crevices a scented milky-leaved shrub about five feet high, with bell clusters of pink flowers veined with red, swayed in the breeze of the river, and filled the place with a secret loveliness."

"And I then ran down the northern slopes . . . among little springs of water, lavender-like Nepeta, campanulas, an aromatic sage-like plant they generally call Benj, and flowerless plants of iris. I pulled one up for its roots . . . which they call Sirish."

"Valleys of the Assassins" (Penguin Books, 1952). Freya Stark.

Chapter 15

The Phenylethyl Esters and Phenylacetates

THE average organic text-book says little about Phenylacetic Acid, other than to record its discovery by Cannizzero in 1855, and to state that it is also known as *alpha*-toluic acid, crystallises in lustrous plates, melts at 76° C., boils at 262° C., is obtained synthetically from benzyl cyanide and forms benzoic acid on oxidation. Regarding its position in perfumery, interest first centres upon its odour. The consensus of opinion agrees to a peculiar hybrid aroma of sweet honey linked by a floral bond to that of a diluted civet, but from my notes upon samples from many sources over a number of years, I find the odour shows considerable variation.

My impression upon opening a tin containing several pounds of the average perfumery grade of phenylacetic acid is the honey note associated with warm maple syrup, but I can always detect a " medicated chemical " back note. I think the true odour is best assessed by the boiling water test, removing the thin cake which separates on cooling, drying and noting the aroma on slightly warming at the edge, and then observing that of the cold saturated solution.

In an imaginative way, it may perhaps be surmised that the rose-hyacinth note of the floral background of phenylacetic acid may owe its osmical association to the contiguous phenylethyl alcohol and phenylacetaldehyde, but I would observe that, viewed as *alpha*-toluic acid, it may also borrow something from the odour-pattern of the toluidines, which are very similar to the quinolines, some of which exhibit a pronounced honey-civet note.

It is also noteworthy that the natural occurrence of phenylacetic acid in the free state seems limited to traces in neroli bigarade and the *arvensis* mints, and regarding the latter, it is interesting to compare the herbal-minty nuance of these with that of the water-cresses, to which the odour of benzyl cyanide is so largely contributory, and to remark that traces of benzyl cyanide (also known as phenylacetic nitrile) may