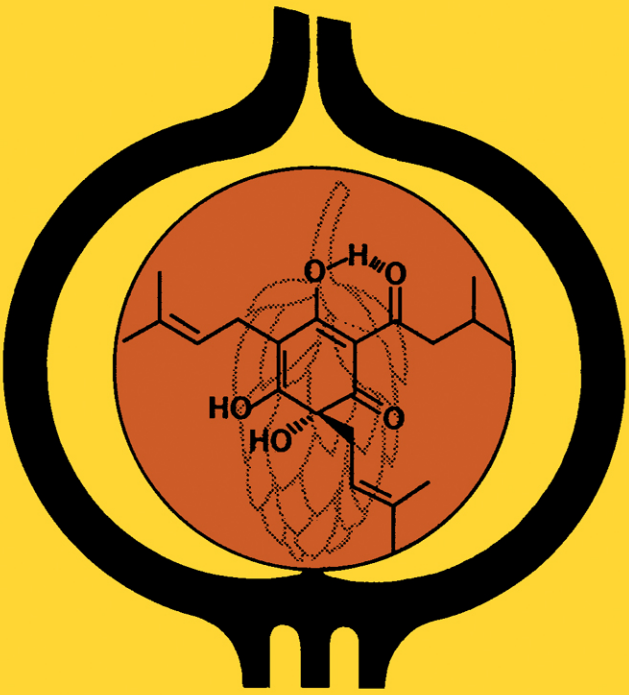
Developments in Food Science

27

CHEMISTRY AND ANALYSIS OF HOP AND BEER BITTER ACIDS

M. VERZELE
D. DE KEUKELEIRE



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PREFACE

Hop chemistry started about 100 years ago when Hayduck, Lintner and Schnell extracted hops and isolated alpha and beta fractions, which had acidic properties. The desire to analyze quantitatively these hop components was thus already obvious.

A second burst of activity occurred in the period 1910-1925 with the work of Wöllmer and Wieland, leading to the elucidation of the structural characteristics of the hop bitter acids. After these achievements, interest slacked off again.

The Laboratory of Organic Chemistry of the University of Gent picked up the thread in 1945, followed by the Brewing Research Foundation at Nutfield in Great Britain. Results were soon forthcoming, which initiated a real research boom in this field with many scientific publications on hop chemistry from laboratories all over the world.

The greatest progress became possible only with the advent of better separation techniques (Counter-Current Distribution-CCD and Gas Chromatography-GC) and with the application of the new spectrometric techniques (especially NMR). In the nineteen sixties and seventies this led to the isolation and structural elucidation of a vast number of hop bitter acids and derivatives. An important result was the fairly complete understanding of the fate and chemistry of the hop bitter acids in the brewing process. The fecundity of this small specialized area of organic chemistry is remarkable. The Laboratory of Organic Chemistry of the State University of Gent alone has published about 150 papers on the chemistry and analysis of hops.

More recently, however, the world output of papers on hop chemistry has dwindled practically to zero. Since 1980, only six, relatively short papers, have been published, all on minor and obscure oxidation products. However, much remains to be done and hopefully a new active period will develop soon. Therefore, it is appropriate to review the present state of knowledge of the chemistry of hop bitter acids and to indicate possible ways for further development. This is the main reason for writing this book.

The content of the book draws heavily on the work of our laboratory, particularly on the chemistry of hop bitter acids, to an extent which may seem excessive to some readers, especially compared to chapters on general aspects of hops and on the analysis of bitter acids. These are indeed far from complete and even more reflect our subjective views. A book covering all aspects of hops science would, however, fill several volumes as large as the present one. The botanic aspects, the harvesting,

conditioning, extraction and storage aspects of hops are only briefly mentioned. The chemistry of certain specific hop fractions, such as the essential oils (dry hopping) or polyphenols, is not even touched upon.

We have included practical, fully detailed procedures on the preparation and/or the separation of many of the compounds discussed. It is hoped that these may serve as a starting point for a future generation of research chemists, picking up the thread again. Indeed, many aspects of hop chemistry are still unknown. In beer there are dozens of as yet uncharacterized compounds derived from hops, which, even though present in very small amounts (ppb or even lower), probably contribute to the beer flavour. This is a challenge for the future.

The chapters on bitter acids analysis do not claim to overview the literature, which has become very complex indeed. In the last ten years alone, about fifty papers have been published on the Liquid Chromatography (LC) of hop bitter acids. Practically every interested laboratory has developed its own procedure. That this implies confusion and difficulties is obvious; LC is much more difficult than most chemists seem to realize.

Since we were the first to introduce really high-efficiency Liquid Chromatography of hop bitter acids, this may be a vindication for including these chapters. We also believe that LC or some future form of high-efficiency separation will guide further development. LC is in any case the area which attracts most attention of laboratories still involved in hop research .

The first chapter in this book is concerned with a short, necessarily far from complete review on hops in general. The last chapters are about the analysis of hop bitter acids. The bulk of the book is about the chemistry of the bitter acids of hop and beer, and this section of the book covers the literature up to the end of 1990.

The last chapter looks at the future and at what could or should be done in hop chemistry. A fairly large list of topics which are worthwhile studying is presented. This could very well be the most interesting chapter for readers involved in laboratory work and who are interested in furthering hop chemistry and hop utilization.

Much time and effort was devoted to the index at the end of the book. It is expected that this index will serve as a reference library-dictionary to hops, hop and beer bitter acids chemistry and analysis.

Gent, July 1991

M. Verzele / D. De Keukeleire

CONTENTS

CHAPTER 1
HOPS AS A RAW MATERIAL IN THE BREWERY

1.1. OCCURRENCE OF HOPS.

Hops are grown for commercial purposes in most of the moderate climate zones of the world. Hop growing areas are situated between latitudes 43°-54° (Europe), 38°-51° (North America), 38°-51° (Japan) in the Northern hemisphere and between 37°-43° (Australia), 41°-42° (New Zealand), 35°-40° (Argentina) in the Southern hemisphere. Wild growing hops are also found in these parts of the world.

The largest hop growing areas are situated in the South-East and Mid-West of England, the Saaz and Auscha districts of Czechoslovakia, the Hallertau region of Germany, the Slovenian parts of Yugoslavia and in the states of Washington, Oregon and California in the United States of America.

Hop needs a fertile soil and specific climatic conditions, especially with respect to the length of the days and the summer temperature. The amount of rain and groundwater is also rather critical for successful cultivation of hop. The hop is therefore one of the most difficult plants to raise.

1.2. ORIGIN AND HISTORY.

Hop or *Humulus lupulus* finds its origins as a wild plant in Europe and Western Asia. Plinius in his "Naturalis Historia" mentions the hop as early as the first century A.D. as a garden plant, grown for its flowers and for its shoots, and which were (and are) eaten as a kind of asparagus. Hops apparently grew between the willow trees "like a wolf between sheep". This explains the name *'Lupus salictarius'* the Romans used, from which the later name *Humulus lupulus* is derived. Hop was used in brewing by the Sumerians and Egyptians as far back as 3000 years ago. The Babylonians and Philistines knew beer, but whether they used hops is not certain.

Hop then disappeared from the scene and only came back much later. Pepin the Short mentions hops in a Donation Act of the year 768. In the 8th and 9th century, cloisters and monasteries (for example the Abbey of Freising in Bavaria) possessed large hop gardens. Hops were then primarily used for medicinal purposes. Documents of the year 822 indicate that monks of Picardy reintroduced the use of hops in brewing when they founded the Corbay cloister on the Weser in Northern Germany. From the 12th and 13th century hops were used extensively in the breweries of Germany. The