CLXXII.—*The Higher-boiling Constituents of the Essential Oil of Hops.*

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In my earlier work on the essential oil of hops (J., 1895, **67**, 54) comparatively small quantities of the oil were used, and consequently the amount of high-boiling fractions, that is, of fractions boiling at temperatures above the boiling point of humulene, was so small as to render their examination impossible.

Through the kindness of Messrs. White, Tomkins and Courage, Ltd., I have had placed at my disposal a quantity of these high-boiling fractions obtained by them in the rectification of hop oil on the large scale. This residue consisted of a dark, viscous oil having an odour differing appreciably from that of ordinary hop oil. Having been dried by heating gently in a current of carbon dioxide, it was distilled under a pressure of 4 mm., and three fractions were collected, b. p. 80—150°, 150—180°, and 180—210° respectively. On further fractional distillation the following seven fractions were obtained :

Fraction.	B. p.	$n_D^{20°}$.	$d_{20°}^{20°}$.	Fraction.	B. p.	$n_D^{20°}$.	$d_{20°}^{20°}$.
1	87— 97°	1·4769	0·8948	5	140—150°	1·4960	0·9389
2	97—110	1·4900	0·9091	6	150—180	1·4969	0·9469
3	110—130	1·4940	0·9328	7	180—200	1·4975	0·9560
4	130—140	1·4950	0·9379				

Fraction No. 1 (b. p. 87—97°).—This reacted strongly with sodium and was found to contain a considerable proportion of saponifiable substances. It was therefore heated with a slight excess of alcoholic potash, and the unsaponifiable oil which remained was separated, dried, and redistilled, the boiling point rising from 65° to 120°. This oil was then esterified in the usual manner by treatment with phthalic anhydride, the portion which resisted esterification being separated and submitted to a fractional distillation. Three fractions were obtained boiling at 76—85°, 85—90°, and 90—98°/4 mm., respectively. Fraction No. 1 reacted vigorously with sodium and on the addition of semicarbazide gave a small quantity of a crystalline substance which, after recrystallisation from light petroleum, melted at 98° (Found: C, 66·8; H, 10·1; N, 17·0. $C_{14}H_{25}ON_3$ requires C, 66·9; H, 9·9; N, 16·8%). From the above formula it would appear that the reacting carbonyl compound must have had the formula $C_{13}H_{22}O$. The molecular weight of the substance regenerated from the semicarbazone was found by the cryoscopic method to be 190 ($C_{13}H_{22}O$ requires M, 194). This substance had a pleasant odour, and b. p. 74—76°/3 mm., $d_{20°}^{20°}$ 0·8861, $n_D^{20°}$ 1·485, and $[\alpha]_D$ − 0·4°. It appears to be a new ketone, for which I suggest the name *luparone*, but unfortunately the quantity obtained was so small that further examination was impossible.

Fraction No. 2 (b. p. 97—110°).—This consisted almost entirely of humulene, and the small amount of liquid having a higher boiling point than that of humulene was added to the next fractions.

Fractions Nos. 3, 4 *and* 5 (b. p. 110—150°).—The general characteristics of these three fractions having proved to be similar, they were mixed and submitted to further fractionation. Four fractions were obtained boiling from 122—174°/3 mm. The densities (20°/20°) of these ranged from 0·9310 to 0·9398, the refractive indices (20°) from 1·4925 to 1·4950, and the rotations from + 2·3° for the lowest fraction to — 1·2° for the highest.

As all these fractions reacted with alkali, it was thought that esters or other saponifiable substances might be present, and the mixed fractions were therefore heated with a slight excess of alcoholic potash. Investigation showed that the disappearance of the alkali was due not to the hydrolysis of esters, but to the decomposition of some substance with the formation of an acid. Treatment with potash was therefore discontinued, and the portion which had resisted the action of the alkali was submitted to further examination. A portion of this was acetylated quantitatively and was found to contain an alcohol. The remainder was heated for 8 hours at 140° with an excess of phthalic anhydride in an atmosphere of carbon dioxide. The mixture was cooled and extracted with a dilute solution of caustic soda and the aqueous portion was evaporated and heated with an excess of alcoholic potash. The alcohol so obtained was again treated in the same manner with phthalic anhydride, and after separation as before was distilled. The greater part boiled at 125—128°/3 mm. and had the following properties. It was a very viscous, colourless, odourless liquid which showed no tendency to crystallise even when cooled in a mixture of solid carbon dioxide and ether; it had $d_{20^\circ}^{20^\circ}$ 0·9738, $n_{D}^{20^\circ}$ 1·5023, $[\alpha]_{D}^{20^\circ}$ — 3·7° (Found : C, 81·7 ; H, 11·1 ; *M*, cryoscopic in benzene, 225. $C_{15}H_{24}O$ requires C, 81·8; H, 10·9% ; *M*, 220). When it was heated with phenylcarbimide, a urethane was obtained which crystallised from dilute alcohol in small needles, m. p. 157° (Found : C, 77·6 ; H, 8·6 ; N, 4·3. $C_{22}H_{29}O_2N$ requires C, 77·8; H, 8·5; N, 4·1%). The alcohol was unsaturated, uniting readily with an amount of bromine corresponding with the presence of one ethylenic linkage. It also appears to be a new compound, for which I suggest the name *luparenol.* This name and the names of two other new compounds described in this paper have been based upon a Spanish word *lupar* (the hop) in order to avoid confusion with various compounds, the names of which have been derived from the Latin designation *humulus lupulus.*

The liquid remaining after the removal of the unsaturated sesquiterpene alcohol gave an intense red colour with ferric chloride, and apparently therefore contained a phenolic substance. It was, however, very difficult to isolate this, since it formed with alkali a salt which decomposed on treatment with water. In addition to this, there was evidence of the presence of a substance having the properties of a tertiary alcohol, from which the phenolic substance could not be completely separated. Attempts to prepare derivatives by treatment with ordinary reagents failed to give any result, and it was therefore decided to resort to the preparation of the silver derivative. The phenol was purified as far as possible by further treatment with phthalic anhydride and subsequent fractionation and from the purified substance a silver salt was prepared by the addition of an alcoholic solution of silver nitrate. An oily liquid resulted which solidified after a few hours. This was separated, washed, and treated with dilute sulphuric acid for the regeneration of the phenol. On steam distillation, the phenolic substance obtained was a pale yellow, mobile oil, having a slight but pleasant odour, b. p. 122—124°/2 mm., $d_{20^\circ}^{20^\circ}$ 0·9170, and $n_D^{20^\circ}$ 1·4942. It was optically inactive (Found: C, 76·6; H, 10·6; *M*, cryoscopic in benzene, 246. $C_{16}H_{26}O_2$ requires C, 76·8; H, 10·4%; *M*, 250). For this substance, which has the general characters of a phenolic ether, I suggest the name *luparol*. It gave an intense red coloration with ferric chloride in alcoholic solution. When boiled for some hours with 50% aqueous potash, it underwent gradual decomposition with the formation of *iso*valeric acid and, among other products, a phenol. *iso*Valeric acid appeared also as the chief product when the substance was oxidised with aqueous potassium permanganate. A very small quantity of the phenol was obtained, b. p. 115—117°/4 mm., $d_{20^\circ}^{20^\circ}$ 0·9448, $n_D^{20^\circ}$ 1·4670 (Found: C, 73·2; H, 9·2. $C_{11}H_{16}O_2$ requires C, 73·3; H, 8·9%). The molecular weight in benzene was, however, considerably higher than that required by the above formula.

Fractions Nos. 6 *and* 7 (b. p. 150—200°).—These, which were very small fractions, gave an intense red coloration with ferric chloride and were found to consist chiefly of the phenolic ether mixed with a proportion of the sesquiterpene alcohol. There was also a small quantity of some very viscous compound which probably consisted of the polymerisation products of myrcene.

The original oil contained a certain amount of free acid, which was removed by shaking with dilute aqueous potash before the investigation above described was commenced. These acids were liberated, and distilled. Silver salts having been prepared and analysed, the greater part was found to consist of *iso*valeric acid, but other acids—which owing to the small quantity of the material available could not be identified—were present in smaller proportions.

It seems very probable from these results that the *iso*valeric acid, and possibly also the other acids mentioned above, had been formed partly, at least, as the result of the oxidation of the phenolic ether, and this may well account for the presence of this acid in old hops.

The difficulties experienced in separating and purifying the substances described above have been considerable, owing chiefly to the very small proportions in which they occur in the essential oil, and the work would have been impossible but for the kind co-operation of Messrs. White, Tomkins and Courage, Ltd. These substances are, in fact, frequently present in nothing more than traces in commercial hop oil, and at the most occur in some specimens to the extent of a few units %. Notwithstanding this, there can be little doubt that they do at times modify the odour of the oil.

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