metal surfaces in contact. It is possible that such a layer is easily broken up, especially on soft metals where plastic deformation at the points of real contact is relatively great. Alternatively, it may be sufficiently thin to permit migration of metallic atoms with the formation of a complete bond.

We thank the Metropolitan-Vickers Electrical Co., Ltd., for the gift of an induction furnace, and the Ministry of Supply for support.

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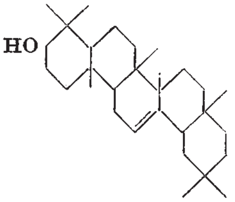
[1] Bowden and Hughes, *Proc. Roy. Soc.*, A, **172**, 263 (1939).

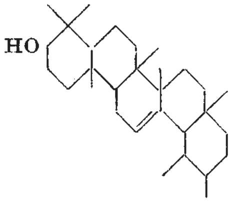
Structure of the Triterpenes: an Interrelationship between the Lupeol and the β-Amyrin Series

Due mainly to the extensive and brilliant researches of Ruzicka and his school, a large majority of the well-characterized triterpenoid compounds have been classified as being related to one or other of the three isomeric alcohols, α-amyrin, β-amyrin or lupeol, and their relationships with these three parent compounds have been rigorously established[1]. Such a grouping is also indicated by the results of studies of molecular rotation differences[2].

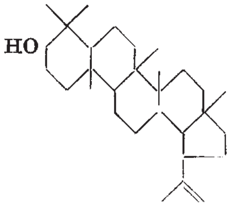
The structures of the three parent compounds have yet to be finally established. Most progress has been made in studies with β-amyrin, and structure (I), originally suggested by R. D. Haworth[3], is now favoured for this compound. For α-amyrin, which is generally similar in many of its properties to the β-isomer, the closely related structure (II) has been proposed[4].



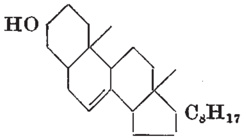
β-Amyrin (I)



α-Amyrin (II)



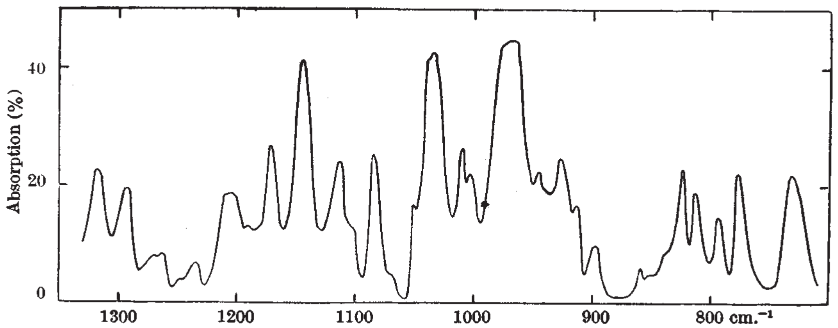
Lupeol (III)



Δ^7-Cholestenol (IV)

The properties of lupeol, on the other hand, especially in so far as the unsaturated centre is concerned, differ rather sharply from those of the amyrins. Various structures have been proposed; but the amount of evidence available to date has scarcely justified more than very tentative formulations. However, representation by formula (III) can now be said to explain the majority of reactions of compounds of this series.

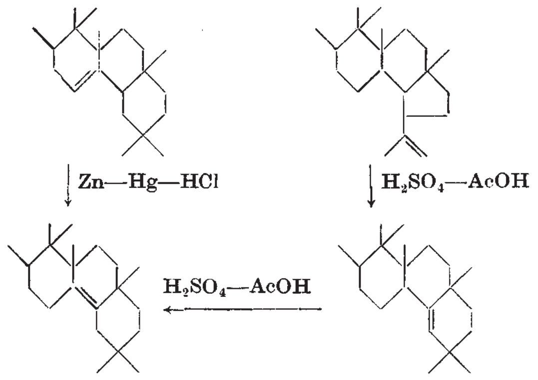
In attempts to convert lupeol derivatives into compounds more susceptible to degradation by conventional methods, isomerization reactions under the influence of acidic reagents have been studied. After a prolonged investigation of the reaction conditions, it has been found possible to isolate two isomerides in *c.* 40 per cent yields from the treatment of lupenone with sulphuric acid in acetic acid – benzene solution. Under the mildest conditions, that is, at 20° for seven days, lupenone is converted into lupenone-I, which on further treatment with the same reagents gives lupenone-II, also obtained under more vigorous conditions directly from lupenone. When the carbonyl group of lupenone-II is converted to a methylene group by the Wolff–Kishner procedure, a hydrocarbon, lupene-II, m.p. 191–192° (corr.) $[\alpha]_D^{20°}$ — 34°, is obtained. This hydrocarbon has been found to be identical with β-amyrene-III, obtained by Winterstein and Stein[5], either by reduction of β-amyrone with amalgamated zinc and hydrochloric acid or by isomerization of β-amyrene-IV with the same reagents. No melting-point depression was observed with a mixture of lupene-II and the hydrocarbon prepared by Winterstein and Stein's procedure, and the infra-red spectra (see diagram) determined in 'Nujol' paraffin were indistinguishable. In addition, it may be noted that the infra-red spectrum indicates that the ethylenic linkage in lupene-II must be of the tetra-alkyl substituted type.



Infra-red spectrum of lupene-II (β-amyrene-III)

The rearrangements which are believed to be involved in the formation of this common hydrocarbon from both β-amyrin and lupeol are indicated in the accompanying partial formulation. Much evidence in support of this scheme has already been obtained and will be published elsewhere in due course. Assuming that β-amyrin is correctly represented by (I), then it seems highly probable that representation of lupeol by (III) will prove to be satisfactory. It can certainly be said that the carbon skeletons and stereochemistry of rings *A*, *B* and *C* are identical in the two series.

The double-bond migrations involved in the interconversions indicated above seem to be closely akin to those well known to occur in rings *B*, *C* and *D* in the steroid series. In fact, we believe that the analogy between β-amyrin and the Δ^7-stenols (for example, IV) will prove to be exceedingly close, and that this correlation with the steroid series will result in a



rapid final solution of the remaining details of triterpene structure.

We are most grateful to Dr. H. P. Koch and Miss J. M. Fabian, of the British Rubber Producers' Research Association, for carrying out the infra-red examination.

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[1] For summaries, see Spring, F. S., Ann. Rep. Chem. Soc., **38**, 192 (1941). Noller, C. R., Ann. Rev. Biochem., **14**, 383 (1945).

[2] Barton, D. H. R., and Jones, E. R. H., *J. Chem. Soc.*, 659 (1944).

[3] Haworth, R. D., Ann. Rep. Chem. Soc., **34**, 327 (1937).

[4] Cf. Meisek, A., Jeger, O., and Ruzicka, L., *Helv. Chim. Acta*, **32**, 1075 (1949).

[5] Winterstein, A., and Stein, G., *Ann.*, **502**. 223 (1933). (On repetition of this work, we find for β-amyrin-III, m.p. 190–191° corr. $[\alpha]_D^{20°}$—28°.)

Molecular Rotation Contribution of C(17) in the Steroid Skeleton

Fieser and Fieser[1] have recently deduced molecular rotation contributions for the various asymmetric centres in the steroid skeleton. Their values for the contribution of C(17) were obtained, in the absence of data permitting direct comparison, from the molecular rotation of cholestane by subtracting the contributions of all the other asymmetric centres, some of which (those of C(9), C(10) and C(13)) appear to be unreliable.

The rotation contributions (Δ) of C(17) can now be estimated more simply and reliably by comparing the molecular rotations, $[M]_D$, of androstane, 5-*allo*-pregnane and 5-*allo*-17-*iso*pregnane, the last-named compound having recently been prepared by Casanova and Reichstein[2].

$[M]_D = [\alpha]_D \times$ mol. wt./100 ; all values are determined in chloroform

Compound	Grouping at C(17)	$[M]_D$	Δ	Ref.
5-*allo*Pregnane	CHEt (β)	+ 52°		2, 3
Androstane	CH_3	+ 5°		4
Contribution of C(17) carrying a (β)-ethyl group			+ 47°	
5-*allo*-17-*iso*Pregnane	CHEt (α)	− 95°		2
Androstane	CH_3	+ 5°		4
Contribution of C(17) carrying an (α)-ethyl group			− 100°	

The contributions of C(17) thus calculated are not equal in magnitude, presumably owing to vicinal action of the asymmetric centres at C(13) and C(14). The values for the contributions of C(17) calculated indirectly by Fieser and Fieser (± 35° for β- and α-substituents respectively) are of the same sign and the same order of magnitude as those given above.

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[1] Fieser, L. F., and Fieser, M., "Natural Products related to Phenanthrene", 211 (3rd edit. New York; Reinhold, 1949).

[2] Casanova, R., and Reichstein, T., *Helv. Chim. Acta*, **32**, 647 (1949).

[3] Ruzicka, L., Goldberg, M. W., and Hardegger, E., *Helv. Chim. Acta*, **22**, 1294 (1939).

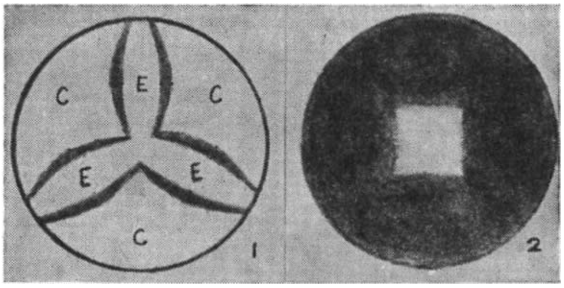
[4] Prelog, V., Ruzicka, L., and Wieland. P., *Helv. Chim. Acta*, **27**, 66 (1944).

Reactivity of Different Faces of a Copper Single Crystal

By using single-crystal metal spheres, Hausser[1], Tamman and Sartorius[2], and in particular A. T. Gwathmey[3] and his collaborators, have demonstrated the marked differences in the physico-chemical properties of the surfaces of a crystal. I have extended their techniques to reactions in which crystals may be etched by vapours. A single crystal of the substance under examination is allowed to react with gaseous reagent under conditions of temperature and pressure such that the product is volatilized away as fast as it is formed. For example, a single crystal of pure copper was electrolytically polished and subjected to the action of a halogen vapour at 444° C. and about 1 mm. pressure. Under the conditions of the experiment the cuprous halide sublimed away continuously, leaving a clean, etched copper surface. Etch pits were produced with their reflecting surfaces (micro-facets) parallel to certain crystallographic planes, so that, on rotating the sphere in a parallel beam of light with the eye looking along the beam, reflexions were seen at certain orientations. It was thus possible to identify easily the facets produced and, by roughly comparing the intensities of the reflected beams, to judge which predominated.

In general, the facets exposed were (111), (011), (012) and (001). In all cases the reflexions from (111) and (011) were strong and that from (001) very weak. With iodine and bromine the (012) reflexion was also strong; but with chlorine it was weak.

Normally the facets were not uniformly distributed, but arranged in patterns as with etching by acids, etc. These patterns were related to the symmetry of the crystallographic axes concerned. Two typical examples are shown diagrammatically.



Copper single-crystal spheres, electrolytically polished, then etched by bromine at 444° C. (1) View along (111) direction with illumination by beam of light parallel to that direction. The regions marked *E* are the 'cube edge' areas and are centred on the (011) poles. The regions marked *C* are 'cube face' areas and are centred on the (001) poles. Both reflect light back along the (111) direction. The dark areas, which do not reflect in this direction, are centred on the (012) poles. (2) View along (001) direction similarly illuminated. Only a small square diffuse patch reflects light back