X-ray patterns may be due to drying conditions and to the effect of buffer in sample F.

Here again, species II may be similar to one of the double hydroxides reported by Feitknecht, since the number of atoms of magnesium and aluminum in species II does add up to five. However, species II has a sulfate moiety in the formula which the double hydroxides apparently lack.

The evidence citable in support of the existence of species I is based on (*a*) the phase solubility diagram shown in Fig. 20 and (*b*) the X-ray diffraction pattern in Fig. 25. The results of the data shown in the reference diagram indicate that species I required a combination of high hydrogen ion, high buffer, and low residual magnesium ion concentrations. These prerequisites are met in the system as designated by half and open circles in Figs. 20 and 21. Figure 21 shows clearly the presence of an invariant plateau in each of the systems with pH values of 8.12 and 8.32. These two curves indicate approximate atomic Mg:Al ratios of 1:2, which correspond to that of the solid species I.

It should be explicitly pointed out that in these studies no serious attempt was made to determine the extent of participation of singly charged ions other than H^+ and OH^-. Acetate, chloride, sodium, and other ions present probably were coprecipitated to varying degrees. It appears likely, however, that their presence does not seriously alter the qualitative nature of these findings.

The results of the present investigation, nevertheless, appear to show that the hydrous-sulfated magnesium aluminate system could very well exist in a number of solid species with different stoichiometric ratios. They also serve to illustrate the value of phase solubility studies in delineating complex inorganic systems.

REFERENCES

(1) Remy, H., "Treatise on Inorganic Chemistry" vol. I, Elsevier Publishing Co., New York, N. Y., 1956, p. 355.
(2) Gordon, N. E., Wiley, R. C., Starkey, E. B., Flenner, A. L., and Lichtenwalner, D. C., *Science*, **54**, 581(1921).
(3) Lichtenwalner, D. C., Flenner, A. L., and Gordon, N. E., *Soil Sci.*, **15**, 157(1923).
(4) Pariselle and Laude, *Compt. Rend.*, **181**, 116(1925).
(5) Zolotukhin, V. K., *Acta Univ. Voronegiensis*, **9**, 69(1937); through *Chem. Abstr.*, **32**, 6971(1938).
(6) Abich, H., *Pogg. Ann.*, **23**, 305,335(1831); through Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," vol. V, Longmans, Green and Co., London, 1924, p. 294.
(7) German pat. 70,175; through U. S. pat. 2,923,660, Feb. 2, 1960.
(8) Prasek, J., *Collection Czech. Chem., Commun.*, **2**, 661(1930).
(9) Quartaroli, A., *Gazz. Chim. Ital.*, **44**, 418(1914); through *Chem. Abstr.*, **9**, 31(1915).
(10) Batta, G., and Baiverlin, J., *Silicates Ind.*, **18**, 5, 60, 97(1953); through *Chem. Abstr.*, **47**, 7754(1953).
(11) Cole, W. F., and Hueber, H. V., *ibid.*, **22**, 75(1957).
(12) U. S. pat., 2,923,660, Feb. 2, 1960.
(13) Feitknecht, W., and Gerber, M., *Helv. Chim. Acta*, **25**, 131(1942).
(14) Feitknecht, W., *ibid.*, **25**, 555(1942).
(15) Feitknecht, W., and Held, F., *ibid.*, **27**, 1495(1944).
(16) U. S. pat. 2,570,532, Oct. 9, 1951.
(17) Beekman, S. M., presented to the Scientific Section, A.PH.A., Chicago meeting, April 1961.
(18) Guttman, D., and Higuchi, T., THIS JOURNAL, **44**, 668(1955).
(19) Welcher, F. J., "Organic Analytical Reagents," vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1947, p. 285.
(20) Schwarzenbach, G., "Complexometric Titrations," Interscience Publishers Inc., New York, N. Y., 1957, p. 62.
(21) Flaschka, H. A., "EDTA Titration," Pergamon Press, New York, N. Y., 1959, p. 75.
(22) Lindstrom, F., and Diehl, H., *Anal. Chem.*, **32**, 1123(1960).
(23) Lewis, L. L., and Melnick, L. M., *ibid.*, **32**, 38 (1960).
(24) Blaedel, W. J., and Meloche, V. W., "Elementary Quantitative Analysis," Row, Peterson and Company, Evanston, Ill., 1957, p. 220.
(25) Klug, H. P., and Alexander, L. E., "X-Ray Diffraction Procedures," John Wiley & Sons, Inc., N. Y., 1954, pp. 163, 324.

Triterpene Constituents of *Sarcostemma viminale* R.Br.

By JOHN D. TORRANCE and JOHANNES L. C. MARÁIS

The isolation of three triterpenes from a benzene extract of *Sarcostemma viminale* by alumina chromatography is described. Two of the triterpenes were identified as β-amyrin and friedelin, but the third, which occurred in the plant as an acetate, could not be identified with any known triterpene acetate. The monohydroxy-triterpene obtained by hydrolysis of the acetate has been designated viminalol.

SARCOSTEMMA VIMINALE is a leafless, glabrous, fleshy climbing plant belonging to the natural order *Asclepiadaceae*. The plant, which has numerous round-jointed stems and a slightly bitter milky latex, is found throughout Central and Southern Africa (1, 2) where it has been used medicinally by various tribes, both as an emetic and as a galactogogue (3). Steyn (4) found *Sarcostemma viminale* to be poisonous, and the plant is thought to be responsible for stock losses in southwest Africa (5).

Received April 18, 1962, from the Department of Chemistry, University of the Witwatersrand, Johannesburg, South Africa.
Accepted for publication August 7, 1962.
John D. Torrance expresses his gratitude to the South African Council for Scientific and Industrial Research for bursaries in 1959 and 1960.

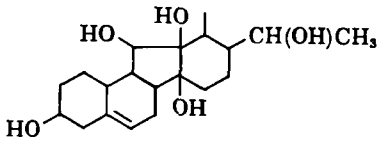
TABLE I.—PHYSICAL CONSTANTS OF SUBSTANCE *D*, *β*-AMYRIN AND THEIR ESTERS

	Substance *D*, ° C.	*β*-amyrin, ° C.
M.p.	198–199	199–200
Acetate m.p.	241–243	241
Benzoate m.p.	233	236

TABLE II.—PHYSICAL CONSTANTS OF SUBSTANCE *C*, FRIEDELIN, AND THEIR DERIVATIVES

M.p.	Substance *C*, ° C.	Friedelin, ° C.
M.p.	261–263	263–263.5
Na/propanol redn. prod.	298–299	301–304
$LiAlH_4$ redn. prod.	281–282.5	278–282
Clemmensen redn. prod.	239–240	246–249
Acetate of Na/propanol redn. prod.	313–315	315–316
Acetate of $LiAlH_4$ redn. prod.	265–267	275–276

A similar plant, *Sarcostemma australe*, thought to be responsible for stock losses in Queensland (6), has been investigated by Earl and Doherty (7) who isolated *α*- and *β*-amyrin from it. A saponin also extracted from *Sarcostemma australe* was shown to be a glycoside of an aglycone containing benzoyl and cinnamoyl groups (8). Cornforth and Earl called the hydrolysis product of the saponin "sarcostin." Reichstein, *et al.*, who obtained sarcostin from *Asclepias giancophylla* (9) and from the roots of *Pachycarpus lineolatus* (10), proposed a C-nor-D-homo-skeleton for sarcostin which enabled Cornforth (11) to propose the following structure for this substance



RESULTS AND DISCUSSION

Sarcostemma viminale, collected in midwinter from the Loskop dam area, was minced and oven-dried before extracting with benzene. The extract was evaporated to dryness, and after redissolving the residue in the least possible volume of benzene it was chromatographed on a basic alumina column. A waxy substance *A*, an amorphous solid *B*, and two crystalline substances *C* and *D* were obtained.

Elementary analysis and micro-Rast molecular weight determinations gave the formula $C_{30}H_{50}O$, for both the crystalline substances *C* and *D*. From this formula it seemed probable that both substances belong to the triterpene group.

The infrared absorption curve of *D* has a broad band at 3333 cm.$^{-1}$ indicating the presence of an associated hydroxyl band (12); further bands at 1035 cm.$^{-1}$ and 996 cm.$^{-1}$ as well as an inflection at 1026 cm.$^{-1}$ indicated an equatorial -3-hydroxy group (13). A trisubstituted ethylenic linkage was indicated by bands at 825 cm.$^{-1}$ and 813 cm.$^{-1}$ (14). The presence of this center of unsaturation was also suggested by the pale yellow color which *D* gave with tetranitromethane. The acetate and

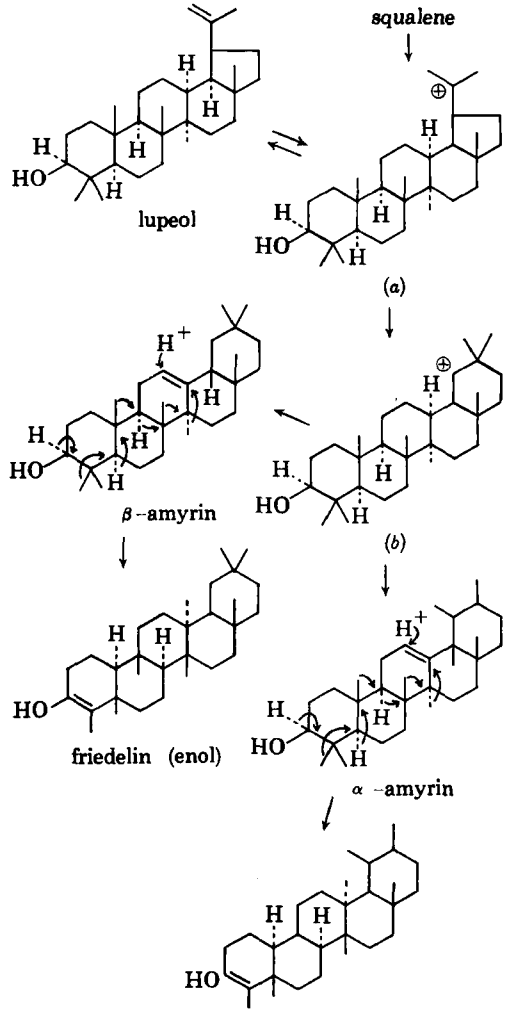


Figure 1.

TABLE III.—ANALYSIS OF COMPOUNDS

	Rast MW.	Empirical formula	Analysis Calcd, % C	Calcd, % H	Found, % C	Found, % H
Viminalol	442	$C_{30}H_{50}O$	84.50	11.74	84.05	11.61
Substance *C*	432	$C_{30}H_{50}O$	84.50	11.74	84.20	11.67
Substance *D*	446	$C_{30}H_{50}O$	84.50	11.74	84.09	11.79
Clemmensen redn. of *C*		$C_{30}H_{52}$	87.37	12.62	86.90	12.45

benzoate of *D* were prepared and from the physical constants of *D* and its esters it was concluded that *D* was β-amyrin (see Table I).

The melting point of β-amyrin showed no depression on admixture with *D* and the infrared absorption curve of an authentic sample of β-amyrin was identical with that of *D*.

The infrared curve of *C* had a sharp intense peak at 1706 cm.$^{-1}$ indicating the presence of a six-membered-ring ketone (15); no bands indicating either hydroxyl groups or unsaturation were present. Substance *C* gave no color with tetranitromethane, suggesting a saturated structure for substance *C*.

Clemmensen reduction of *C* gave the corresponding hydrocarbon $C_{30}H_{52}$. The keto group was reduced with lithium aluminum hydride and also with sodium/propanol, to give two different alcohols. The acetates of both alcohols were prepared, and from the physical constants of these compounds it was concluded that *C* was friedelin (see Table II).

An authentic sample of friedelin gave an infrared absorption curve identical with that of substance *C* and its melting point showed no depression on admixture with *C*.

It is of interest to find both β-amyrin and friedelin in the same plant since the friedelin series of compounds can be derived from the β-amyrin series by a sequence of 1:2 shifts of methyl groups and hydrogen atoms away from ring *A* toward ring *E*.

Corey and Ursprung (16, 17) have shown this relationship to exist by converting friedelin-3β-ol into olean-13-(18)-ene using various acidic reagents to bring about the multigroup rearrangement.

The same authors suggest that a possible biosynthetic pathway to friedelin in the plant is as shown in Fig. 1. The intermediate (*a*) which is originally derived from squalene can undergo a Wagner Meerwein rearrangement to give, by way of the intermediate (*b*), either α- or β-amyrin. β-Amyrin, in turn, is converted into friedelin and theoretically α-amyrin should undergo a similar transformation to form an as yet unknown derivative of friedelin.

If this biosynthetic scheme is valid, lupeol should also be found in *Sarcostemma viminale*. We have not been able to isolate lupeol, but the amorphous acetate *B* appeared to belong to the lupeol series.

This amorphous solid, after being rechromatographed in hexane on a basic alumina column, had a melting point of 160–162° but could not be crystallized. The infrared absorption curve indicated the presence of an isopropenyl group (bands at 3069 cm.$^{-1}$, 1639 cm.$^{-1}$, and 878 cm.$^{-1}$) (18) and an acetoxy group (bands at 1730 cm.$^{-1}$ and 1247 cm.$^{-1}$) (19), as well as a trisubstituted double bond (bands at 826 cm.$^{-1}$ and 808 cm.$^{-1}$) (14).

The amorphous powder was hydrolyzed with alcoholic potash to give the corresponding alcohol, m.p. 176–178°. Elementary analysis indicated the empirical formula $C_{30}H_{50}O$ for this alcohol. Since the alcohol could not be identified with any of the known triterpene alcohols, the name viminalol has been assigned to it.

The infrared curve of viminalol has a broad band at 3322 cm.$^{-1}$ indicating an associated hydroxyl group (12), further bands due to the hydroxyl group at 1036 cm.$^{-1}$, 1024 cm.$^{-1}$, and 903 cm.$^{-1}$ indicated that the hydroxyl group was most probably situated at the C-3 position of the triterpene skeleton (13). The absorption curve also showed that the isopropenyl group and the trisubstituted double bond were still present in viminalol. The latter observation was also indicated by the pale yellow color which was obtained with tetranitromethane.

The amorphous compound *B*, which must be viminalol acetate, took up one mole of hydrogen on hydrogenation in glacial acetic acid with Adam's catalyst to yield a product melting point 172–178°, which could not be crystallized. The infrared curve of this reduction product showed that the isopropenyl group was no longer present.

It is possible that viminalol acetate may be similar in nature to scandol (20, 21), which was originally reported as a new triterpene, but which was later found, by Corey, *et al.* (22), to be a mixture of β-amyrin and lupeol.

Further work is in progress to identify viminalol and substance *B*.

REFERENCES

(1) Phillips, E. P., "The Genera of South African Flowering Plants," 2nd ed., University of South Africa, Department of Agriculture, Botanical Survey No. 25, 1951, p. 605.
(2) Thiselton-Dyer, W. J., "Flora Capensis," Vol. 4, Section 1, L. Reeve & Co., London, 1909, p. 755.
(3) Watt, J. M., and Breyer-Brandwijk, M. G., "The Medicinal and Poisonous Plants of Southern Africa," E. & S. Livingstone, Edinburgh, 1932, p. 150.
(4) Steyn, D. G., *Onderstepoort J. Vet. Science Animal Ind.* **9**, 114(1937).
(5) Adellar, private communication.
(6) Gilruth, J. A., and Murnane, D., *J. Council Sci. Ind. Research Australia*, **4**, 58, 225(1931).
(7) Earl, J. C., and Doherty, *ibid.*, **10**, 26(1937).
(8) Cornforth, J. W., and Earl, J. C., *J. Chem. Soc.*, **1939**, 737.
(9) Nascimento, J. M., Jager H., Tamm C., and Reichstein, T., *Helv. Chim. Acta*, **42**, 661(1959).
(10) Abisch, A., Tamm, C., and Reichstein, T., *ibid.*, **42**, 1014(1959).
(11) Cornforth, J. W., *Chem. Ind. London*, **1959**, 602.
(12) Bellamy, L. J., "The Infrared Spectra of Complex Molecules," Methuen., London, 1954, p. 84.
(13) Allsop L., Cole, A. R. H., White, D. E., and Willix, R. L. S., *J. Chem. Soc.*, **1956**, 4868.
(14) Bellamy, L. J., "The Infrared Spectra of Complex Molecules," Methuen, London, 1954, p. 31.
(15) Bellamy, L. J., *ibid.*, p. 114.
(16) Corey, E. J., and Ursprung, J. J., *J. Am. Chem. Soc.*, **77**, 3668(1955).
(17) Corey, E. J., and Ursprung, J. J., *ibid.*, **78**, 5041 (1956).
(18) Bottomley, W., Cole, A. R. H., and White, D. E., *J. Chem. Soc.*, **1955**, 2624.
(19) Bellamy, L. J., "The Infrared Spectra of Complex Molecules," Methuen, London, 1954, p. 153.
(20) Cook, D. L., Parks, L. M., Dunker, M. F. W., and Uhl, A. H., THIS JOURNAL, **33**, 15(1944).
(21) Cook, D. L., Parks, L. M., Dunker, M. F. W., and Uhl, A. H., *ibid.*, **33**, 18(1944).
(22) Corey, E. J., Preskow, S., and Parks, L. M., *ibid.*, **46**, 183(1957).